

Pre-Lithiation Technology for Rechargeable Lithium-Ion Batteries: Principles, Applications, and Perspectives

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Lithium-ion batteries (LIBs) have been widely used as a new energy storage system with high energy density and long cycle life. However, the solid electrolyte interface (SEI) formed on the surface of anode consumes excess active lithium during the initial cycle, resulting in an initial irreversible capacity loss (ICL) and reducing the overall electrochemical performance. To solve the critical issue, pre-lithiation technology has been accepted as one of the most promising strategies. Due to the pre-lithiated treatment provides additional active lithium to compensate for

the ICL and effectively improves initial Coulombic efficiency (ICE), leading to raising the working voltage, increasing the Li⁺ concentration, as well as improving the energy density and cycle stability of LIBs. In this overview, the causes of ICL in LIBs are analyzed from different perspectives, and various pre-lithiation strategies are systematically classified and summarized. Finally, some current problems and development prospects in this field are summarized, with prospects for realizing industrialized technologies.

1. Introduction

Energy storage has become a critical global issue due to the irreversible and rapid consumption of fossil fuels and the consequent severe environmental pollution. The development of new renewable energy sources and clean energy systems has become an essential task, and the utilization of new sustainable and environmentally friendly energy sources such as wind and solar power has attracted great attention in the past decades.^[1–4] However, these types of renewable energy systems are affected and limited by the uncertainty of external conditions, thus there is an urgent need to explore high-performance energy storage devices. Among them, recharge-

able secondary lithium-ion batteries (LIBs) with high energy density, long cycle life and high lithium reserves, together with no memory effect have been successfully used in many applications, including the small battery market for portable electronics and electric vehicles, as well as large-scale grid storage.^[5–12] Commercial LIBs usually exhibit energy densities of 250~300 Wh kg⁻¹ with 1000 lap cycles at the battery level. In this regard, it is necessary to improve the electrochemical properties such as energy density and cycle life of LIBs, which are important for the future development of new energy storage devices and the protection of the global environment.^[13–19]

The storage and release of electric energy in LIBs are attributed to the transfer of Li ions between the cathode and anode during the charging and discharging processes. However, after longer cycles, the usable energy content of the battery decreases, resulting in the irreversible capacity loss (ICL). The ICL of LIBs is primarily due to the following aspects: microcellular interaction between the anode active material and the electrolyte, leading to self-discharge reactions; formation of the solid electrolyte interface (SEI); decomposition reactions of the electrolyte and the solvent; loss of active material and the presence of various defects. In particular, not all active Li ions are transferred in the next cycle, about 6~15% of Li ions are irreversibly consumed to form a SEI layer.^[20–26] The SEI layer is electric insulating and ionic conductive, thus preventing direct contact of the anode with the electrolyte and over decomposition of the electrolyte. Despite the fact that the repeated growth and destruction of the SEI layer cause a large consumption of active Li ions.^[27–32] In addition, volume expansion of the active material and cracking of the surrounding matrix causes a sharp rise in the internal resistance during Li ions extraction, which leads to isolation of the active particles and unfinished de-lithium reaction, resulting in dead lithium not continuing to circulate.^[33–37] Moreover, the embedding and detachment of Li ions between the anode and cathode creates

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a high density of defects on the surface of the alloy particles, the interface or the grain boundaries, which results in the Li ions will be irreversibly trapped at the defect sites with strong bonds of fewer coordination atoms. To solve these issues, it is necessary to supply extra active Li ions to compensate for irreversible Li loss in LIBs.^[38–42]

Pre-lithiation, as an effective strategy to address the issue of active Li loss and increase the energy density of LIBs, is based on the principle of using a specific pre-lithiation process to provide extra active lithium to the LIBs before the initial cycle (Figure 1a, b). In addition to complementing the Li loss caused by the constructing of initial SEI layer, it also efficiently controls the formation of a stable SEI layer, improving the initial Coulomb efficiency (ICE) and cycling stability.^[43–51] Generally, there are some methods known for pre-lithiation at the electrode level, including chemical pre-lithiation, electrochemical pre-lithiation, and additive pre-lithiation, whereas not enough researches and summaries for pre-lithiation are available in addition to these electrode level, such as electrolyte pre-lithiation, separator pre-lithiation, binder pre-lithiation, and so on.^[52–55] Therefore, a comprehensive review with a focus on pre-lithiation technologies for achieving supplemental active lithium is just around the corner.

In this overview, these pre-lithiation strategies are classified mainly according to the pre-defined location of the lithium source (anode, cathode, separator, electrolyte, and extra components), which summarizes the recent progress of pre-lithiation technology and discusses the merits and limitations of various pre-lithiation strategies (Figure 2). Moreover, we have looks into the practical pre-lithiation strategies for future research and applications. This work aims to interpret the pre-lithiation strategies to provide new insights into the development of LIBs, furthermore, it is informative for the pre-sodiation or other preprocessing strategies for secondary energy storage technologies. Pre-lithiation technology is also an effective strategy to increase the energy density of batteries.



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2. Anode Pre-Lithiation Strategy

Since the ICL of LIBs is mainly due to the irreversible electrochemical processes on the surface of anode, supplementing the anode material with a lithium source is the most direct pre-lithiation strategy. Depending on the mechanism and method of replenishing active lithium, the strategy of direct pre-lithiation of anodes can be divided into three main aspects: anode pre-lithiation additives, electrochemical pre-lithiation, and chemical pre-lithiation, respectively.

2.1. Anode Pre-Lithiation Additives

The main principle of the anode pre-lithiation additives strategy is to bring forward the introduction of Li ions into the anode materials, and the whole process is based on the potential difference between the electrode and the reagent to drive the Li ions to embed into the main structure of the anode, so that the pre-lithiation process can be completed. For the anode pre-lithiation additives, a high theoretical Li ion capacity and sufficient redox potential are required to avoid reducing the output voltage of the LIBs. The anode pre-lithiation additives can be in various forms, such as stabilized lithium metal powder (SLMP), lithium alloy compounds and composites, etc., all of which have the above characteristics.^[56–63]

As an additive for the pre-lithiation of the anode, lithium metal is generally used directly in SLMP to compensate for the ICL of the anode. This pre-lithiation strategy of using lithium metal directly as an additive does not introduce other impurities in the process, while only the passivation layer that may exist on the surface will exert better stability. Generally, SLMP are prepared by directly using lithium metal as a raw material for melting while a stable passivation film of Li_2CO_3 is generated on the metal surface, but the high chemical reactivity may cause safety hazards. There are two main methods of pre-



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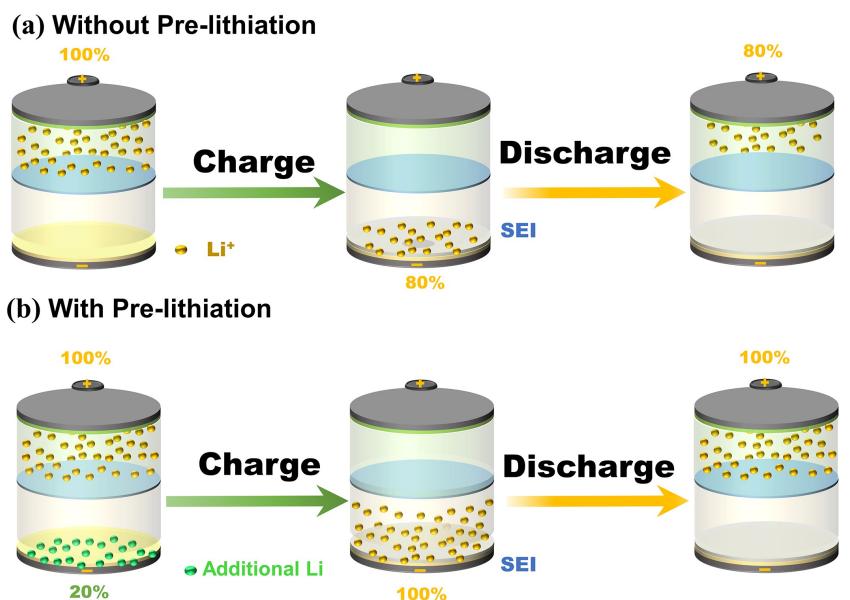


Figure 1. Schematic diagram of the initial cycle process of lithium-ion batteries (a) without pre-lithiation and (b) with pre-lithiation.

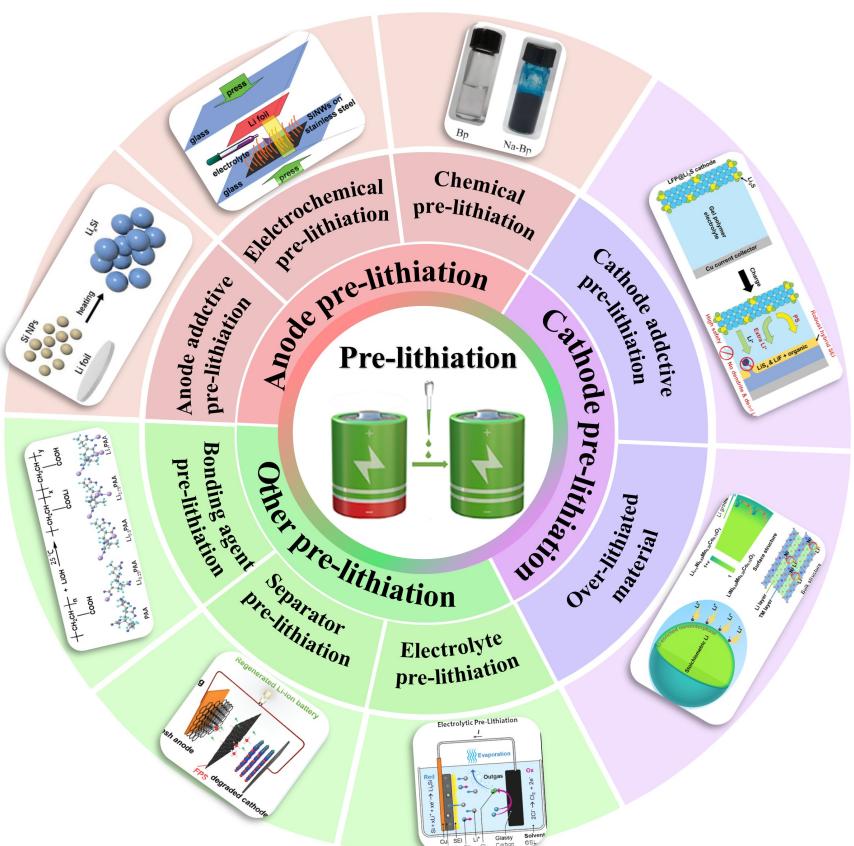


Figure 2. Schematic diagram of pre-lithiation strategies for LIBs.

lithiation using SLMP: 1) Sprinkle SLMP directly on the surface of the anode and then activated under pressure in the presence of electrolyte.; 2) Add SLMP as additives in the process of making a mixed slurry.

When using SLMP as a pre-lithiation additive, in order to improve the air stability, it is usually stabilized by mixing with other reagents to achieve stabilized lithium replenishment. By mixing SLMP with styrene butadiene rubber (SBR) and toluene (SST for short), SLMP can be used as a stabilized pre-lithiation

reagent to achieve safe and controlled pre-lithiation. SLMP was the main pre-lithiation reagent, and SBR contributed to the uniform dispersion of SLMP in toluene.^[64] The pre-lithiation process mainly achieves lithium transfer by lowering the configured pre-lithiation reagent on the surface of SiO anode and applying pressure activation (Figure 3a). By controlling the volume of SST, the extent of pre-lithiation can be easily controlled within a certain range to achieve an ICE of 66~120%. Similarly, SLMP was homogeneously blended with SBR and polystyrene (PS) as a lithium-rich and stabilized polymer binder, which bonded SLMP firmly to the anode surface and could be easily activated by applying calendering pressure.^[67] By using SLMP pre-lithiated anodes, the electrochemical performance of full cells was improved. Alternatively, uniformly mixed pre-lithiation of SLMP powders and silicon oxide powders can be achieved after activation by milling, and lithium replenishment using this research method was used to increase the ICE of the half-cell from ~48% to 90% and to increase the energy density of the full cell.^[68]

Lithium alloy compounds, as an additive for anode pre-lithiation, are generally used to pre-lithiate the anode material by forming a stable alloy layer of lithium metal and non-metal particles through a certain chemical reaction process. A pre-lithiation strategy to form lithium-silicon alloy nanoparticles (Li_xSi NPs) by thermal alloying reaction of silicon (Si) nanoparticles (NPs) and lithium (Li), and then chemically reacted isopropoxyaluminum with Li_xSi to form a $\text{Li}_x\text{Al}_y\text{SiO}_z/\text{Li}_2\text{O}$ protective layer (A- Li_xSi NPs) on the surface of Li_xSi as a Si-based anode pre-lithiation (Figure 3b).^[61] The additive effectively improves the ICE of the anode material. The experimental results show that when 6.4% of A- Li_xSi NPs is added, the ICE is increased by 14%, and that the open circuit voltage (OCV) of the anode is reduced from 2.5 V to about 0.8 V. As OCV is an indicator to detect the degree of pre-lithiation, the successful pre-lithiation leads to the early formation of the SEI layer on the

silicon anode. This pre-lithiation strategy of adding the lithium source directly to the silicon anode not only serves as a direct active material, but also improves the electrochemical performance of the LIBs and compensates for the ICL. Similarly, a pre-lithiation strategy that forms a protective layer of lithium-rich compounds on the anode surface can improve its air stability. It was shown that the surface modification method using 1-fluorodecane reduction of the Li_xSi surface to form a continuous dense coating could enhance the stability of Li_xSi NPs.^[65] The artificial coating consists mainly of LiF and lithium alkyl carbonate, which is chemically stable and effective in preventing damage to the alloy layer. (Figure 3c). The Li_xSi NPs protected by the artificial SEI layer exhibited a high capacity of 2100 mAh g^{-1} in dry air, and maintained 1600 mAh g^{-1} capacity in humid air.

Similarly, synthesizing a $\text{Li}_x\text{Si}-\text{Li}_2\text{O}$ core-shell nanoparticle with high specific capacity is an effective strategy due to the relatively poor air stability of Li_xSi , and the $\text{Li}_x\text{Si}-\text{Li}_2\text{O}$ core-shell nanoparticles were produced by a one-step thermal alloying process.^[66] Moreover, $\text{Li}_x\text{Si}-\text{Li}_2\text{O}$ core-shell nanoparticles can be processed in the slurry under the conservation of Li_2O blunt shell and exhibit high capacity (Figure 3d). For this, here showed the compensation of the loss of active lithium by utilizing a mixture of lithium alloys and anodes as an anode material, which consisted of densely arranged Li_xM ($\text{M}=\text{Si}, \text{Sn}, \text{or Al}$) nanoparticles (Figure 4a). Due to the graphene flakes wrapped around the outer layer of Li_xM , it can be stabilized in air and maintains a stable 98% capacity retention and cycling stability even in half cells. (Figure 4c).^[69]

In addition, composites obtained by combining two or more lithium alloys or oxides of lithium could also be applied as a pre-lithiation additive. For example, a pre-lithiation of oxides of group IV elements to synthesize $\text{Li}_{22}\text{Z}_5-\text{Li}_2\text{O}$ composites ($\text{Z}=\text{Si}, \text{Ge}, \text{Sn}$, etc.) has been developed (Figure 4b).^[70] As a pre-lithiation additive for graphite anode and other alloy-based

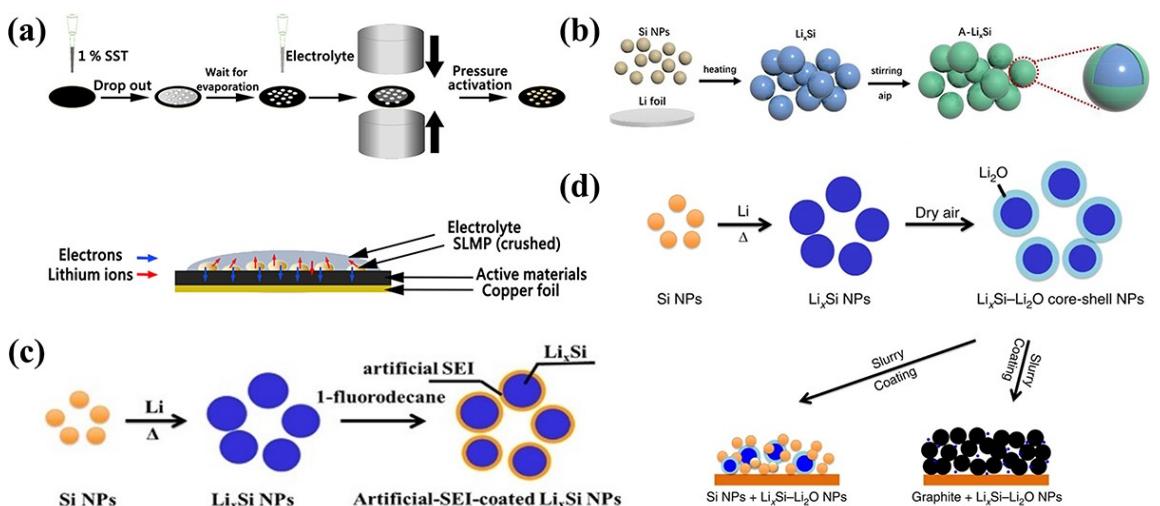


Figure 3. (a) Schematic illustration of pre-lithiation process of the SiO electrode. Reproduced with permission from Ref. [64]. Copyright 2021, American Chemical Society. (b) Synthesis process for the A- Li_xSi . Reproduced with permission from Ref. [61]. Copyright 2021, Elsevier. Diagram of the formation process of (c) artificial SEI-coated Li_xSi NPs. Reproduced with permission from Ref. [65]. Copyright 2015, American Chemical Society and (d) $\text{Li}_x\text{Si}-\text{Li}_2\text{O}$ core-shell NPs. Reproduced with permission from Ref. [66]. Copyright 2014, Springer Nature.

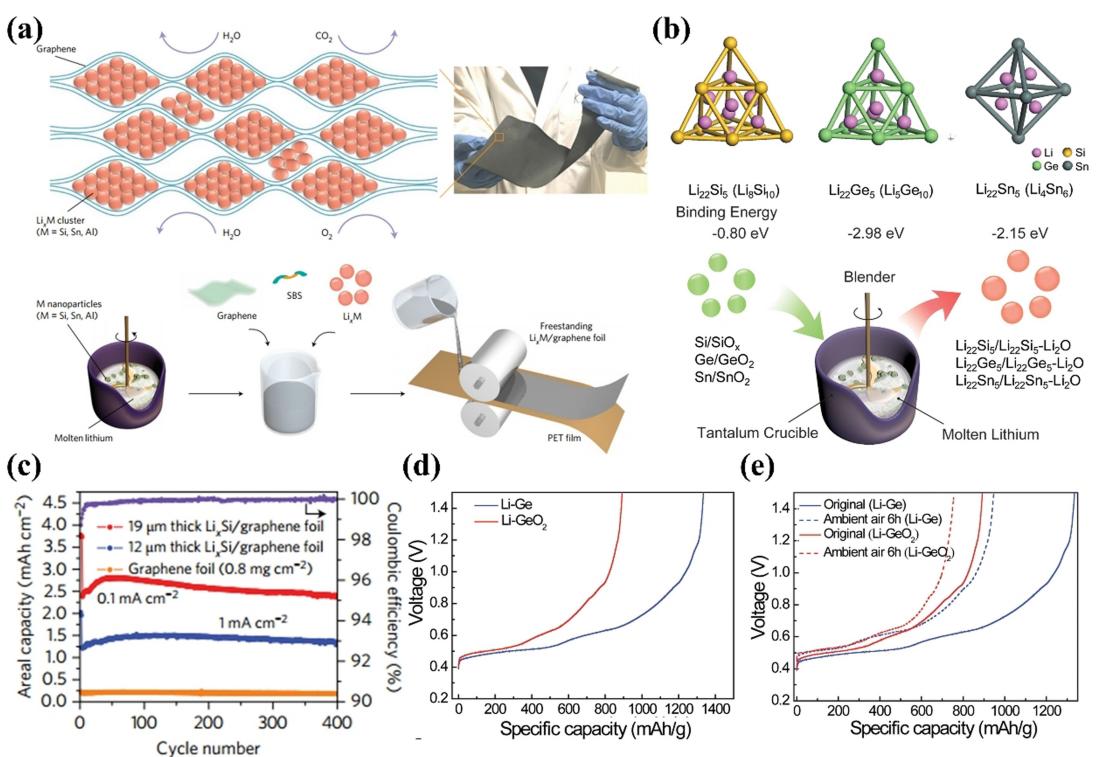


Figure 4. (a) Schematic of the microstructure and fabrication process of the $\text{Li}_x\text{M}/\text{graphene}$ foils. Reproduced with permission from Ref. [69]. Copyright 2017, Springer Nature. (b) Schematic diagram showing a one-pot metallurgical process. (c) The cycling performance of a pure graphene foil. Initial delithiation capacities of pre-lithiated Ge NPs and pre-lithiated GeO_2 NPs (d) before and (e) after exposure to ambient-air condition. Reproduced with permission from Ref. [70]. Copyright 2017, Elsevier.

anode materials, thus to compensate for the ICL of LIBs and to improve ICE. It can be found that Li_xGe NPs as the group IV lithium alloys also had a pre-lithiated capacity of 947 mAh g^{-1} and a capacity retention of 70% with exposure to ambient air for 6 h (Figure 4d, e). The capacity retention is 85% when using $\text{Li}_x\text{Ge}/\text{Li}_2\text{O}$ composites, and the best air stability of Li_xGe relative to other Group IV lithium alloys is mainly since the strongest binding force of Ge and Li atoms in the cubic $\text{Li}_{22}\text{Ge}_5$ crystal. This is precisely caused by the $\text{Li}_{22}\text{Z}_5/\text{Li}_2\text{O}$ composite with uniformly dispersed active Li_xZ , which are embedded in the robust Li_2O matrix allowing more bonding between the oxygen atoms in Li_2O and the lithium atoms in Li_{22}Z_5 , thus effectively inhibiting the oxidation process and increasing its air stability.

It can be concluded that anode pre-lithiation additives, such as lithium powders, lithium alloy compounds, and composites (SLMP, Li_xSi , $\text{Li}_{22}\text{Z}_5/\text{Li}_2\text{O}$ composites), can provide high pre-lithiation capacity and effectively compensate for the ICL. However, these additives suffer from high chemical reactivity and safety hazards, making their application in actual battery assembly lines challenging. To enhance the stability of lithium metal and its compounds in air, artificial intervention is frequently employed to reactively generate a stable passivation film on the surface. This ensures compatibility with the actual production process while fully compensating for the active lithium.

2.2. Electrochemical Pre-Lithiation

The main principle of the electrochemical pre-lithiation method is to transfer lithium using the electrochemical reaction between the anode and lithium metal, which is achieved mainly through two pathways: internal short circuit (ISC) and external short circuit (ESC). The main advantages of this strategy are that the pre-lithiation degree could be precisely adjusted and the whole pre-lithiation process is adjustable by parameters of contact time and pressure, so that it is widely used for pre-lithiation of LIBs. However, the pre-lithiation needs to be performed during the discharge of the half-cell, after which the cell should be disassembled to assemble the full cell, so the operation processes are complex and incompatible with current battery manufacturing.^[71,72]

ISC is regarded as an electrochemical pre-lithiation strategy, in which the anode material is in direct contact with the lithium metal, mainly through a self-discharge mechanism in the electrolyte, which could be using lithium films, lithium strips, etc. The principle of this pre-lithiation strategy is to use the potential difference generated by the direct contact between the anode and the lithium metal to drive the electron transfer to balance the potential, so that the lithium ions are first released into the electrolyte through electron transfer, and then transferred to the anode through the electrolyte to achieve charge balance.^[73] Therefore, this direct contact pre-lithiation method can be used as pre-lithiation for graphite-based, tin-

based and silicon-based anode materials. In addition, the ISC method is also compatible with the current roll-to-roll battery manufacturing process, which is very promising and largely improves the energy density of LIBs. However, it still needs to be used safely in the drying chamber, which is not conducive to large-scale application due to the high price of lithium foil.

A silicon nanowire (SiNW) anode pre-lithiation has been proposed to realize this mechanism of pre-lithiation through the self-discharge mechanism of direct contact between lithium metal and anode. The SiNW anode is bonded directly to a foil of lithium by the action of the electrolyte, and electrochemical pre-lithiation is achieved by short-circuiting when the SiNW contacts the lithium foil under pressure.^[74] Electrons pass through the top of the nanowire when the SiNW is in contact with the lithium foil, while when the SiNW is not in contact with the lithium foil, electrons pass through the contact position and then up through the bottom of the SiNW (Figure 5a, b). The pre-lithiation could be almost completed within 20 minutes, but the anode chemistry after pre-lithiation is highly reactive, which could only complete the pre-lithiation and cell assembly in an inert gas. Moreover, the actual amount of pre-lithiation is difficult to control and the need to remove the lithium foil prior to battery assembly adds to the difficulty and time cost of the operation, so this technology appears to be difficult to apply to commercial battery. Li-Metal foil based is more cost effective in the market than SLMP as well as easier to achieve fast and accurate pre-lithiation. Pre-lithiation with hard carbon anodes in the laboratory was completed within 2 h, which was signifi-

cantly faster than SLMP or lithium strip pre-lithiation, and the incorporation of microspores in the lithium foil improved the electrolyte activity.^[75]

In order to simplify the electrochemical pre-lithiation step, directly in-situ lithium replenishment at the silicon anode is an effective strategy. A principle to design a layer of lithium mesh padded on the silicon anode prior to the assembly of the cell,^[76] and after the addition of electrolyte the pre-lithiation occurs spontaneously between the contacting silicon anode and the lithium mesh according to the short-circuit mechanism (Figure 5c). The experiments were conducted to precisely control the degree of pre-lithiation mainly through the lithium mesh with different porosities. By using the optimized lithium mesh porosity for in-situ pre-lithiation, the ICE of the half-cell was increased from 70% to 100%, and the long-term capacity of the full-cell was increased by more than 30% after 150 cycles. Some researchers have introduced a resistive buffer layer (RBL) through direct contact between the SiO_x anode and the lithium foil to adjust the speed and extent of lithiation (Figure 5d). Note that the porosity structure, soft characteristics and high electric permittivity of RBL is not only promote Li^+ transfer and electron transfer, and the soft characteristics of RBL also ensure close contact to achieve uniform pre-lithiation. The pre-lithiated SiO_x anode provides stable operation of 200 cycles in NCM622// SiO_x full cells.^[77]

In addition, roll-to-roll mechanical methods can also be used to achieve pre-lithiation, a strategy utilized to produce Sn–Na alloy gold foils from sodium and tin to compensate for

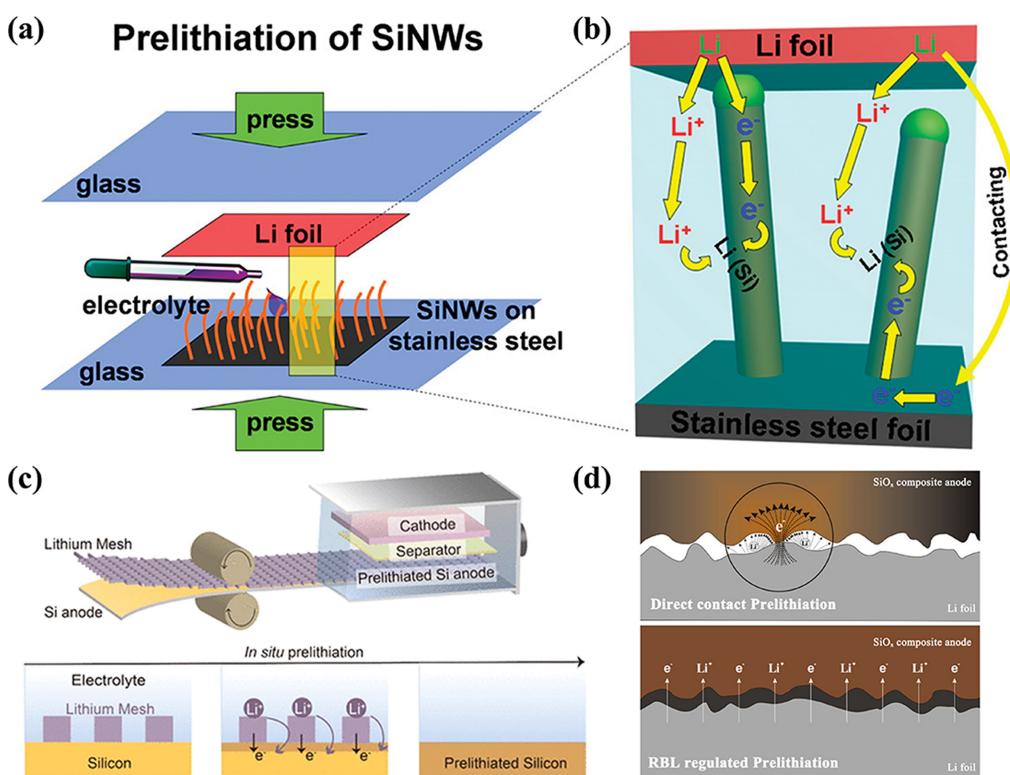


Figure 5. (a, b) The pre-lithiation of SiNWs by IS strategy. Reproduced with permission from Ref. [74]. Copyright 2018, American Chemical Society. (c) Schematic diagram of the composite of lithium mesh and silicon anode. Reproduced with permission from Ref. [76]. Copyright 2023, American Chemical Society. (d) The direct contact pre-lithiation process. Reproduced with permission from Ref. [77]. Copyright 2019, American Chemical Society.

the loss of reactive Na in the subsequent cycle (Figure 6a).^[78] In the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{Na-Sn}$ full cell, the ICE was significantly increased from 25% to 75%, and the average CE could be maintained at 99.44% from the 2nd to the 100th cycle. Similarly, a scalable roll-to-roll process to pre-alloying tin with lithium has been reported, and prepared Li_{x}Sn foils not only exhibited excellent air stability, but also increased ICE from 20% to 94%, and were able to achieve 200 stable cycles in LFP// Li_{x}Sn full cells.^[79] They also utilized the roll-to-roll mechanical pre-lithiation method to pre-lithiated tin foils, aluminum foils and silicon/carbon anodes (Figure 6b, c). The ICE of the prepared Li_{x}Sn foil was increased from 20% to 94%, and 200 stable cycles were achieved in LFP // Li_{x}Sn full cells. Moreover, the Li_{x}Sn foils also showed excellent air stability and excellent cycling performance.

ESC is a pre-lithiation strategy that can regulate the current and measure the voltage. The principle is to realize an external circuit through a half-cell composed of a porous polymer separator isolated from the Li metal and the anode in the electrolyte, which uses the potential difference generated when the contact between the two electrodes drives the transfer of lithium ions to realize pre-lithiation. A resistor or constant current power supply is generally used in the external circuit to control the degree of pre-lithiation, which regulates the formation of the SEI layer on the anode surface as well as the composition to improve the ICE of the LIBs.

In order to apply this strategy, a lithium metal foil-based electrically short-circuited pre-lithiation scheme is compatible with the current roll-to-roll process (Figure 6d).^[80] The experiments use carbon-coated SiO_x ($c\text{-SiO}_x$) as the anode, so that the electrolyte and septum exist between the $c\text{-SiO}_x$ electrode and the lithium metal foil to form an external short circuit, which causes a potential difference between the electrodes to trigger spontaneous pre-lithiation. Moreover, an applied resistance is

introduced to control the rate of pre-lithiation. The SEI layer on the surface of the $c\text{-SiO}_x$ electrode after pre-lithiation is formed by not only lithium carbonate and alkyl lithium carbonate but also more inorganic components such as LiF , Li_2O , Li_3SiO_y , etc., which makes the formed SEI layer more stable.^[81-83] The experimental results show that the ICE of the half-cell after pre-lithiation reaches 94.9% compared with 73.6% of the original un-pre-lithiated cell, and the ICE of the full cell composed of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, a nickel-rich layered cathode material, increases significantly from 58.85% to 85.34% (Figure 6e, f). When cycled at 1 C multiplicity, the pre-lithiated full cell capacity basically remained constant. After 100 cycles, the capacity of the pre-lithiated $c\text{-SiO}_x/\text{NCA}$ full cell decreased 0.92 mAh cm^{-2} , while the original cell capacity decreased from 1.52 mAh cm^{-2} to 1.17 mAh cm^{-2} .

The electrochemical pre-lithiation strategy is highly effective in enhancing ICE and initial ICL. It allows for precise control of the degree of pre-lithiation (current density, time) and can simplify handling steps by being structured as a continuous roll-to-roll procedure. However, the high chemical reactivity of electrochemically pre-lithiated anodes is not stable for storage in air. Therefore, the subsequent manufacturing process of the cell must be carried out under inert gas conditions, which adds to the cost due to the additional electrochemistry and materials involved. Electrochemical pre-lithiation has the potential to achieve industrial scale by optimizing parameter settings, using a stable lithium source, and implementing safety technologies such as the multilayer layer structure and thermal isolation.

2.3. Chemical Pre-Lithiation

Chemical pre-lithiation is the use of a redox pre-lithiation reagent with strong contact with the anode, the resulting redox

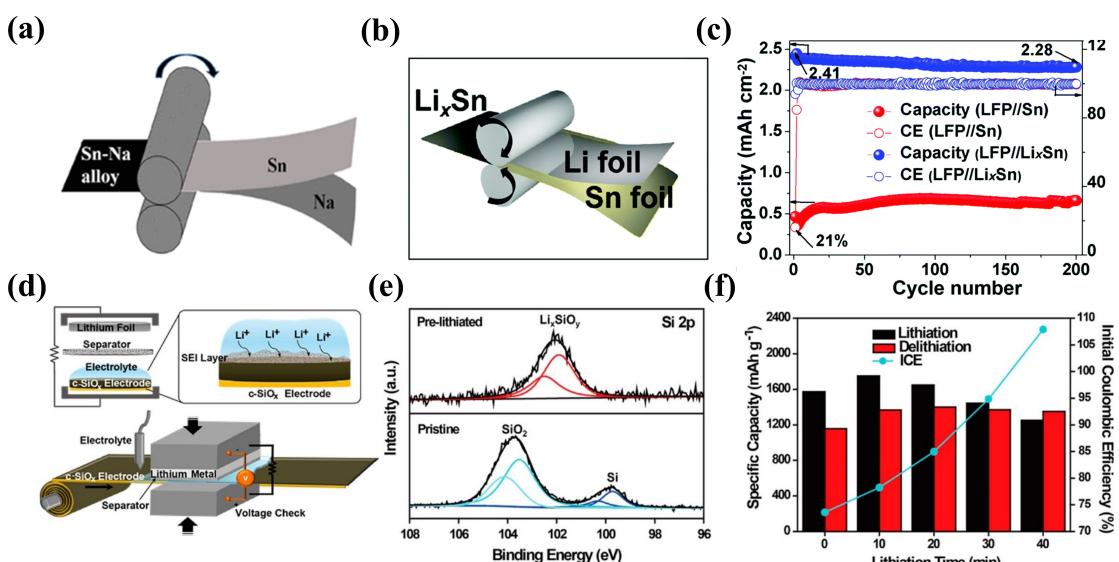


Figure 6. (a) Diagrammatic drawing of the metallurgical pre-alloying process. Reproduced with permission from Ref. [78]. Copyright 2019, American Chemical Society. (b) Illustration of roll-to-roll pre-lithiation method. (c) Capacity and cycle stability in full-cell cycling. Reproduced with permission from Ref. [79]. Copyright 2019, Royal Society of Chemistry. (d) Pre-lithiation process of $c\text{-SiO}_x$ electrode. (e) The XPS spectra of both electrodes. (f) The comparison of the specific capacity and ICE with respect to different pre-lithiation times. Reproduced with permission from Ref. [80]. Copyright 2016, American Chemical Society.

potential difference will transfer the active lithium to anode to complete pre-lithiation. It was found that solution chemical pre-lithiation using reducing chemicals was unable to dose active lithium in silicon-based anodes and only formed SEI layers, thus mitigating part of the cycling irreversibility. A solid SEI layer is formed to protect the anode upon contact with the electrolyte after pre-lithiation, thus improving the electrochemical performance of LIBs.^[84–87] The supply of lithium is accurately controlled in the pre-lithiation process is essential, the level of pre-lithiation is generally controlled by the pre-lithiation time and the redox potential of the reagent. An insufficient pre-lithiation level cannot achieve high ICE, while excessive pre-lithiation can lead to the formation of lithium dendrites during cycling, which leads to the degradation of the electrochemical performance of LIBs. Chemical pre-lithiation is mainly achieved by solution immersion or spraying, where the anode material is directly immersed in a lithium aromatic solution and uniform and spontaneous lithiation of the active particles in the anode occurs.^[88–91]

Pre-lithiation solutions are generally generated by the reaction of lithium metal, aromatic hydrocarbons and there are non-polar solvents (ethers) according to a certain ratio, and the solution color is dark blue or green (Figure 7a). The most studied lithium-biphenyl (Li-Bp) and lithium-naphthalene (Li-Np) both have low redox potentials (≈ 0.33 and 0.35 V vs Li⁺/Li, respectively) and can react with various anodes with high lithiation potentials (e.g. Al, P, Sn, SnO₂).^[96–99] For the pre-lithiation of anodes in lithium-aromatic hydrocarbon (AC) complex solutions, the main principle is to utilize the electro-

philicity of aromatic hydrocarbons to react with lithium metal in an ether solvent to produce lithium-containing aromatic radical compounds (LACs), and then transfer the dissolved Li ions to the anode via a potential difference.^[92] The degree of pre-lithiation can be determined by the time of pre-lithiation and the concentration of the solution. General solvents and organic reagents can be toxic and volatile, so they should be operated in an inert atmosphere. A strategy suggests that the mechanism of chemical pre-sulfurization is due to the high electron affinity of naphthalene.^[93] Experiments used a pre-lithiated solution composed of naphthalene and lithium metal dissolved in butyl methyl ether (BME) to pre-lithiated the SiO anode. It has been found that after 72 h of immersion of the electrode in the pre-lithiation solution, the OCV drops sharply to a very low level and then stabilizes (≈ 0.21 V vs. Li/Li⁺). Later He used the same mechanism but in a different solvent dimethoxyethane (DME) and proposed the pre-lithiation of lithium titanate (Li₄Ti₅O₁₂) and further found that Li₄Ti₅O₁₂ could be successfully pre-lithiated within 3 h (Figure 7b).^[100]

Chemical pre-lithiation is an effective way to improve the ICE of LIBs and compensate for the initial ICL, but the redox potential of the pre-lithiation reagent must be lower than that of graphite (≈ 0.2 V) when graphite is chosen as the anode. Based on the theory of solvation and coordination chemistry, a new solution design strategy is proposed for pre-lithiation by selecting a strongly electron-donating,^[94] site-resistive, and chemically stable solvent to regulate the redox potential of the pre-lithiation reagent and prevent solvent co-insertion during pre-lithiation, which led to the successful pre-lithiation of

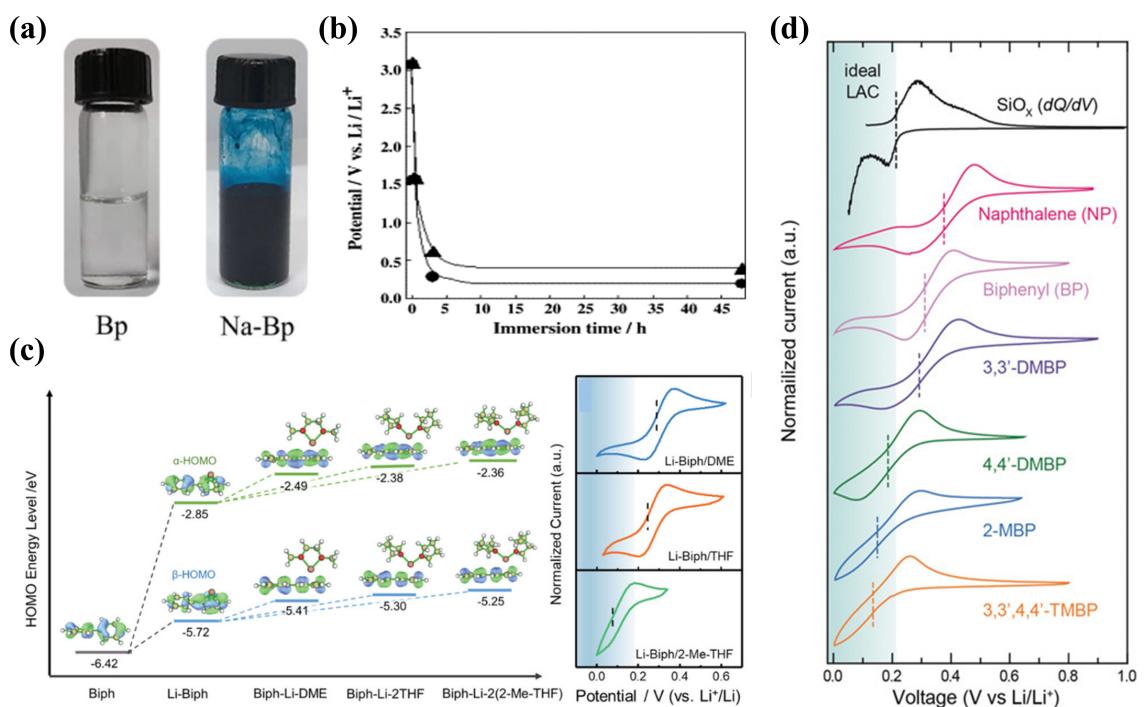


Figure 7. (a) The optical images of sodium-biphenyl (Na-Bp) solution dissolved in DME. Reproduced with permission from Ref. [92]. Copyright 2020, American Chemical Society. (b) The curve of OCV with immersion time after pre-lithiation. Reproduced with permission from Ref. [93]. Copyright 2005 Elsevier. (c) Geometrical configurations and HOMO energy levels. Reproduced with permission from Ref. [94]. Copyright 2021, Wiley-VCH. (d) The cyclic voltammetry profiles of different pre-lithiation reagents. Reproduced with permission from Ref. [95]. Copyright 2020, Wiley-VCH.

graphite anodes (Figure 7c). Experiments using dimethyltetrahydrofuran solution of lithium-biphenyl ($\text{Li-BP}/2\text{-MeTHF}$) as the pre-lithiation solution can pre-lithiate graphite anode to the desired state within minutes without disrupting the lattice structure of the graphite. It was found that the introduction of various electron-giving functional groups ($-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$, and $-\text{OH}$) in the opposite position of the benzene ring can effectively increase the electron density, which reduces the electron affinity and reduction potential. Based on this theory, a strategy has established linkage between the LUMO energy levels of aromatic molecules and the corresponding pre-lithiated reagents,^[95] comparing that substituted methyl (2-Me) at the neighboring position would have a larger potential shift relative to that at the interposition (3,3-2Me) and the para position (4,4-2Me) (Figure 7d), while for the four substituents 3,3,4,4-4MeBP, the redox potential was reduced to 0.129 V, in agreement with the redox potential trend. This reflects the electron effect of the substituent group related to the elevation of the molecular orbital energy level, solving the problem that the SiO_x anode cannot be pre-lithiated with BP and contributing to the practical application of this technology.

The in situ construction of the SEI layer on top of the pre-lithiation will lead to the subsequent cycling performance of the battery. It has been found that the synergistic effect of pre-lithiation and electrolyte additives can be used to optimize the composition of the SEI layer. The in situ formation of a dense and stable LiF-rich SEI layer on the SiO_x anode surface in combination with fluorinated ethylene carbonate (FEC) protected the integrity of the SiO_x particles (Figure 8a). The pre-lithiated SiO_x anode has a high ICE of 90.7% and excellent cycling performance.^[101] Some experimenters have pre-sodiated sodium-ion batteries anode based on a pre-lithiation strategy. For example, a bifunctional sodium dibenzene (Na-DK) pre-

anode was used on the hard carbon (HC) anode., which not only compensated the irreversible sodium uptake on the oxygen-containing functional group that reacted with the carbon defect on the penta/heptad ring to generate quasi-metallic sodium in HC (Figure 8b).^[102] The active sodium ions compensated by the pre-sodiation form a stable NaF -rich SEI layer in HC in advance, which facilitates the interfacial reaction kinetics and stable Na^+ embedding and delinking. In particular, the pre-sodiated HC (pHC) still has a high ICE of 100% and capacity retention of 82.4% after 6800 cycles in the half-cell, and nearly 100% capacity retention after 700 cycles in the full-cell. This work provides insight into chemical pre-lithiation and a new strategy for high-stability sodium-ion batteries.

Similarly, lithium supplemented with pre-lithiation can be used to construct a lithium-containing SEI layer by reacting with the corresponding solution. For example, a new strategy has proposed to construct an artificial hybridized SEI layer consisting of LiF and Li_3Sb in situ through the spontaneous chemical reaction of pre-lithiated SiO_x anode with DME solution of SbF_3 (Figure 8c).^[103] With the adjustable degree of pre-lithiation and immersion process, the SEI layer suppresses the volume change of SiO_x anode, and enhances and regulates the Li^+ diffusion kinetics. The half-cell exhibits excellent electrochemical performance with an ICE of 94.5% and a capacity retention of 77.4%. In addition, the full cell with commercial $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ cathode and modified SiO_x anode had an ICE as high as 86.0% with excellent cycling performance.

Chemical pre-lithiation can reduce the ICL of LIBs and improve their electrochemical performance. It is a commercially promising pre-lithiation strategy due to its rapid lithium replenishment and simple reaction principle. This makes it easy to operate and highly experimentally efficient. However, selecting pre-lithiation reagents with sufficiently low redox

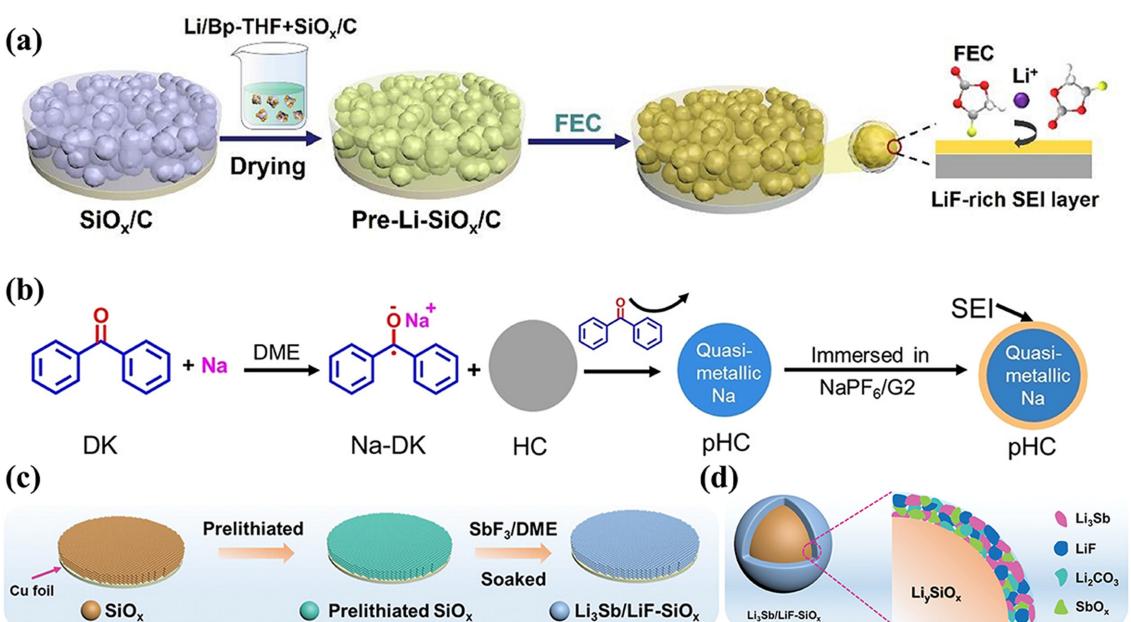


Figure 8. (a) Schematic diagram of the process of pre-lithiation and FEC modulating the SEI layer. Reproduced with permission from Ref. [101]. Copyright 2021, Elsevier. (b) Schematic diagram of chemical pre-sodiation process. Reproduced with permission from Ref. [102]. Copyright 2022, Wiley-VCH. (c) The fabrication process schematic of a series of $\text{Li}_3\text{Sb}/\text{LiF-SiO}_x$. Reproduced with permission from Ref. [103]. Copyright 2023, Wiley-VCH.

potentials is challenging. Additionally, it is important to consider the compatibility of chemical pre-lithiation reagents with conventional battery processes, as well as the safety implications of over-supplementation of lithium. Current strategies for improving chemical pre-lithiation include optimizing the selection and use of pre-lithiation reagents, improving integration with roll-to-roll production processes, combining with other interfacial engineering, and focusing on the formation of the SEI layer during the pre-lithiation process.

3. Cathode Pre-Lithiation Strategy

Different from anode pre-lithiation, cathode pre-lithiation is indirectly pre-lithiated by supplementing lithium into the LIBs system. The cathode pre-lithiation methods in this section are divided into two main types, the first is using pre-lithiation cathode additive and the other is the direct use of extra lithium ions to prepare the over-lithiated cathode materials, both of them can compensate for the ICL during the initial charge process.^[104–107]

3.1. Cathode Pre-Lithiation Additives

The principle of this cathode pre-lithiation additive is based on the migration of Li ions from cathode to anode side during the initial charge process of LIBs, forming a SEI layer and embedding it into the anode lattice. For cathode additives, lithium-rich compounds with high lithium ion giving ability are generally selected, and high Li ions extraction ability and low working potential are required (Figure 9a). These requirements effectively avoid the decomposition of electrolyte and ensure the high stability of the electrochemical energy storage system. The strength of the electron-giving capacity is generally measured by the dischargeable Li ions capacity, which is the difference between the charge capacity and discharge capacity in the range of the cathode cut-off operating potential, which requires a suitable lithium extraction potential for cathode additives. This potential is lower than the maximum anode charge potential of the low working potential, and there is no reversible lithium insertion in the subsequent cycle. The main principle is that after the anode is charged to the lithium extraction potential, Li ions are extracted from cathode additives and embedded in the lattice of the anode or used to build the SEI layer. Generally higher potential cathode additive has better chemical stability than anode additives, and the

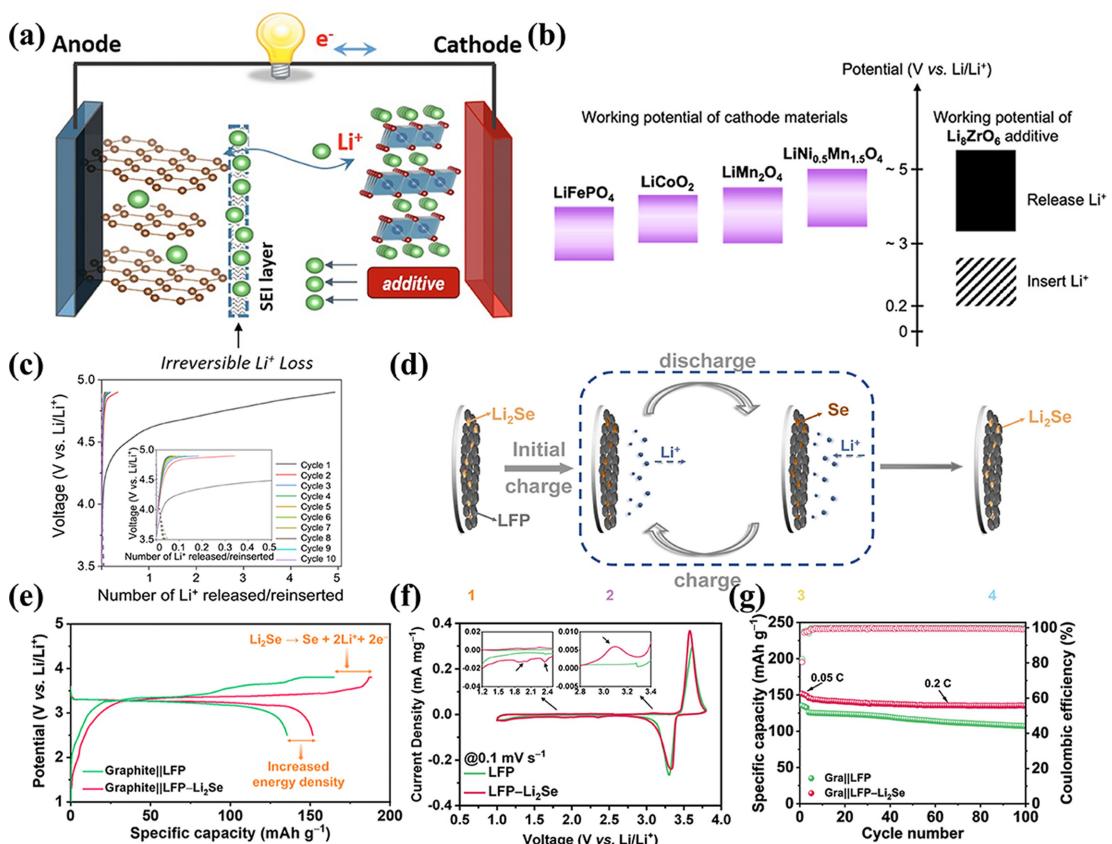


Figure 9. (a) The principle of cathode pre-lithiation method. Reproduced with permission from Ref. [110]. Copyright 2016, Wiley-VCH. (b) Illustration of the working potential ranges, and (c) voltage profiles of the assembled LZO/C half-cell. Reproduced with permission from Ref. [111]. Copyright 2022, American Chemical Society. (d) Schematic illustration of the evolution of the LFP-Li₂Se cathode. (e) The charging/discharging curves, (f) CV curves, and (g) cycle performance of LFP and graphite. Reproduced with permission from Ref. [112]. Copyright 2023, American Chemical Society.

most used are ternary materials, binary materials and composites.^[108,109]

The ternary material $\text{Li}_x\text{M}_y\text{O}_z$ ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}$, etc.) is used as a cathode pre-lithiation additive by extracting Li ions for transfer to the anode to compensate for the consumption of active lithium. A lithium-rich ternary pre-lithiation additive Li_5ZrO_6 (LZO) (Figure 9b), in which each unit contains 8 Li ions, was investigated to provide a large number of Li ions at relatively low mass loading (Figure 9c).^[111] It was shown that the full cell assembled with LZO combined with the cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) and graphite as the anode improved the reversible specific capacity by 15–18% and the capacity retention by 30% in 50 cycles. Moreover, the electrochemical impedance spectra showed that the combined contact resistance of LNMO half-cells were also significantly reduced after pre-lithiation with LZO. The other ternary additives are called “sacrificial” salts, such as $\text{Li}_2\text{C}_4\text{O}_4$ ^[113] and $\text{Li}_2\text{C}_2\text{O}_4$,^[114] which have theoretical capacities between 300 mAh g^{-1} and 600 mAh g^{-1} . The working potential is between 3 and 4 V. After the reaction the lithium salts are converted to gaseous products of N_2 and CO_2 without residues, but these organic additives are not intensively studied at present.

The Li ions capacity provided by binary additive is generally higher than that provided by ternary additive, which is based on the decomposition reaction of lithium compounds. For example, LiN_3 ^[115], Li_3N ^[110], and Li_2O_2 ^[116] exhibit theoretical capacities of 547.4 mAh g^{-1} , $2308.5 \text{ mAh g}^{-1}$, and 1154 mAh g^{-1} , while ternary additives such as Li_2NiO_2 ,^[117] Li_6CoO_4 ,^[118] and Li_2MoO_3 ^[119] capacity is lower than 400 mAh g^{-1} . However, these lithium binary compounds decompose during electrochemical reactions to produce gases, requiring the battery to be sealed

afterward, which is costly in terms of battery manufacturing time and not suitable for commercial application. Lithium selenide (Li_2Se), which can be irreversibly converted to selenium (Se) at 2.5 to 3.8 V to provide extra lithium, is proposed as the cathode pre-lithiation additive for LIBs. Compared with previously reported cathode pre-lithiation additives such as Li_6CoO_4 , Li_2O , and Li_2S , they not only have higher specific capacity and conductivity, but they also avoid gas release and incompatibility with carbonate electrolytes. However, the poor reaction kinetics of the Li_2Se particles in carbonate electrolytes and the lack of a simple method to synthesize Li_2Se nanoparticles lead to less lithium loss from Li_2Se (Figure 9d). To compensate for this deficiency, a pre-lithiation strategy to synthesize Li_2Se nanoparticles by reacting Se particles with Li-Naph solution as a cathode additive. The experimental results showed that the initial charging capacity of the LFP half-cell increased by 14 mAh g^{-1} after the addition of 6 wt% Li_2Se nanoparticles, and the discharge specific capacity of the Gr//LFP full cell increased from 135 mAh g^{-1} to 151 mAh g^{-1} in the first cycle (Figure 9e, f, g), effectively improving the energy density of LIBs.^[112]

Li_2S has been added to commercial LiFePO_4 cathodes as a high lithium content additive to increase the active lithium content. Recently, a design has been reported that a high-energy quasi-solid-state anode-less battery focusing on the naturally high lithium content of Li_2S to provide a source of active lithium, which can undo irreversible lithium depletion without introducing hazardous substances. (Figure 10a).^[122] The lithium polysulfide (LiPS) released from Li_2S further guided the formation more stable SEI layers, reducing irreversible Li losses caused by Li dendrimers and interfacial parasitic reactions. This

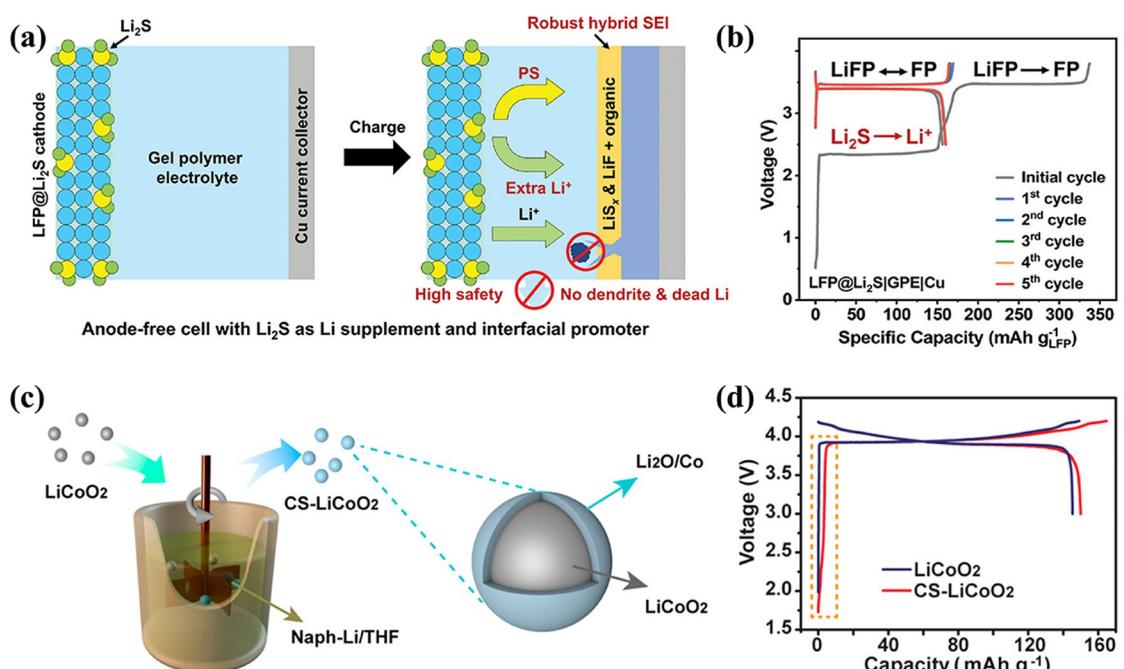


Figure 10. (a) Schematic of an anode-free cell with Li_2S as Li supplement and interfacial promoter. (b) Discharge-charge voltage curves of assembled full cell. Reproduced with permission from Ref. [120]. Copyright 2023, Wiley-VCH. (c) Schematic illustration of the preparation of CS- LiCoO_2 , and (d) the initial cycle charge/discharge curves. Reproduced with permission from Ref. [121]. Copyright 2020, American Chemical Society.

pre-lithiation strategy enables the full cells with a long life of 500 cycles, 46% higher weight energy, 94% higher volume energy, and 22–47% higher volumetric energy than LFP //Li batteries compared to LFP//Gr full cells. (Figure 10b).

Ternary additives are also widely used in cathode pre-lithiation additives, a strategy has reported a built-in pre-lithiation material formed on the surface of LiCoO_2 to compensate for the ICL of the anode.^[121] The chemical reaction between the Naph-Li solution and LiCoO_2 was used to chemically form $\text{Li}_2\text{O}/\text{Co}$ on the surface of LiCoO_2 . It shows a schematic illustration of the process of lithium cobaltate preparation and the structural evolution of the CS- LiCoO_2 cathode during charge/discharge cycles (Figure 10c). It was found that the total charge capacity of LiCoO_2 with 1.5 wt % $\text{Li}_2\text{O}/\text{Co}$ increased by 15 mAhg⁻¹ compared to the pristine LiCoO_2 cathode material due to the irreversible lithium extraction ($4\text{Li}_2\text{O} + 3\text{Co} \rightarrow 8\text{Li}^+ + 8\text{e}^- + \text{Co}_3\text{O}_4$, $2\text{Li}_2\text{O} \rightarrow 4\text{Li}^+ + 4\text{e}^- + \text{O}_2 \uparrow$) (Figure 10d). The experimental results have shown that the full cell assembled with Gr-SiO anode achieves an energy density of 533 Whkg⁻¹, which is 52 Whkg⁻¹ higher than that of the cell using the pristine LiCoO_2 electrode. The discharge capacity of the full cell using LiCoO_2 with core-shell at 0.1 C (2.60 mAhcm⁻²) was 11% higher than pristine LiCoO_2 (2.34 mAhg⁻²), as for stable cell cycling.

The materials obtained by combining metal and binary or ternary materials as cathode pre-lithiation additives changed the reaction mechanism of general binary/ternary additives, which would not only increase the capacity of LIBs and avoid the generation of harmful gases. Recently, Cui's group synthesized $\text{Li}_2\text{O}/\text{metal}$, $\text{Li}_2\text{S}/\text{metal}$, and LiF/metal nanocomposites with high Li ions capacity by a chemical reaction between oxides, sulfides, fluorides, and molten lithium. These Li-containing compounds act as cathode pre-lithiation. The lithium-rich g additives to compensate the active lithium for the LIBs system, thereby improving ICE and cycle stability.^[123] Li_5FeO_4 has good prospects as a cathode pre-lithiation additive with excellent performance and high controllability, but it's very poor air stability and incomplete lithium ion release has led to its limited application. Therefore, a high-temperature solid-phase method to generate a protective layer of Li_6CoO_4 (LCO@LFO) on the surface of Li_5FeO_4 particles, which not only effectively improved the stability of Li_5FeO_4 under ambient atmosphere to improve its electrochemical performance. The result shows that the initial discharge capacity of NCM811 full cell after pre-lithiation (205 mAhg⁻¹) in 2.0 V–4.5 V (vs Li^+/Li) charge/discharge interval is higher than that of the original full cell (166.5 mAhg⁻¹), and the full cell energy density is increased by 14.35%. The modification of this cathode pre-lithiation additive achieves the stability of the LCO@LFO material and increases the commercial utility.^[122]

The use of cathode pre-lithiation additives can effectively compensate the ICL of the battery and improve its electrochemical performance. Binary compound additives with a high redox potential are preferred over lithium-rich ternary compound additives due to their higher specific capacity and stability in air. However, binary compound additives may face obstacles in the reaction process as they can react with the

electrolyte to generate gas or heat. To enhance the potential of cathode pre-lithiation additives, it is crucial to screen additives that exhibit high stability and safety performance, and to improve their stability in air. This is essential for achieving large-scale commercialization.

3.2. Over-lithiated Cathode Material

The direct use of a pre-lithiation strategy with over-lithiated cathode materials, which stores Li ions without adding any extra additives, provides an extra source of lithium to compensate for the irreversible loss in capacity of the anode. Pre-lithiation cathode materials include layered oxygen cathodes and spinel cathode materials, which require a high pre-lithiation capacity to increase the specific capacity of LIBs and need to be charged to 5 V to achieve pre-lithiation.^[124–128] However, the regulation of the pre-lithiation should be reasonably controlled, as the introduction of excessive lithium will deteriorate the structural framework, resulting in poor structural stability. The use of $\text{Li}_5\text{V}_2(\text{PO}_4)_3$ (L5VP) over-lithiated cathode material to match the HC anode by first lithiation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (L3VP) to L5VP, which would release an additional 2 Li ions to be converted to L3VP to compensate for the Li loss (Figure 11a). The results show that the L5VP//HC pouch full cell has an ICE of 96.7% and 320 Whkg⁻¹ specific energy. Moreover, L5VP has zero residue and the prepared cathode maintains excellent electrochemical performance (Figure 11b, c). In addition, L5VP is safe and stable than pre-lithiation methods.^[129]

Some over-lithiated spinel materials have been extensively studied as over-lithiated cathode materials. Johannes Betz *et al.*^[130] obtained over-lithiated cathode materials by pre-lithiation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) by stirring high-pressure spinel LNMO particles and Li metal. The electrochemical analyses demonstrated that the electrochemical accessibility and long-term cycling stability of the batteries were significantly improved after pre-lithiation. The charging and discharging materials have a positive effect on the discharge capacity, energy and capacity retention in both LNMO//Gr and LNMO//Si/C batteries. Comparing the pristine LNMO//Gr with the pre-lithiated LNMO//Si/C cells, with a 21% increase in specific energy.

Among them, The $\text{LiNi}_{0.65}\text{Mn}_{0.20}\text{Co}_{0.15}\text{O}_2$ consisting of a lithium-rich gradient interfacial layer to provide excess electrochemically active lithium to compensate for the Li loss and to improve cycling stability by regulating the Li/Ni disorder in their experiments (Figure 11d). The experimental results show that the over-lithiated cathode material $\text{Li}(\text{Ni}_{0.65}\text{Mn}_{0.20}\text{Co}_{0.15})\cdot\text{O}_2$ (220 mAhg⁻¹) exhibits a charge-specific capacity of 24 mAhg⁻¹ greater than that of the pristine cathode (196 mAhg⁻¹) (Figure 11e), and the full cell energy density is also increased by 11% and cycle stability is improved.^[131]

However, using Li-rich and Mn-rich layered oxides as cathodes can have problems such as capacity degradation and average discharge voltage decay of LIBs during cycling. So a method has been found that using these Li-rich and Mn-rich layered oxides as cathode materials and replacing the propor-

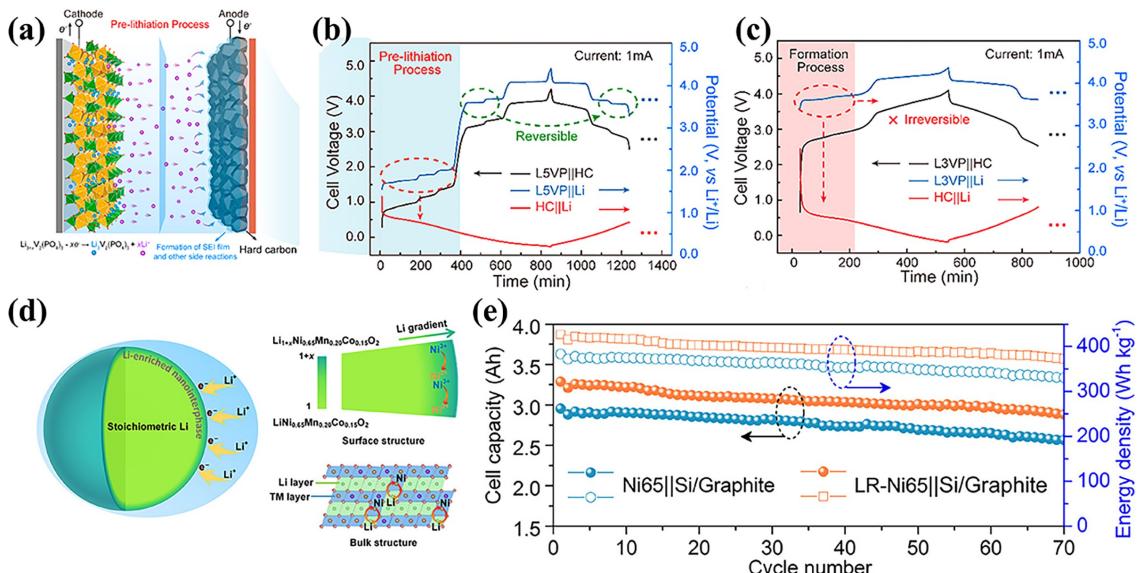


Figure 11. (a) Schematic of the pre-lithiation process of full cell. Voltage curves of (b) the L3VP//HC and (c) L5VP//HC full cell. Reproduced with permission from Ref. [129]. Copyright 2019, Elsevier. (d) Schematic illustration of the topotactic chemical reaction process. (e) Cycling performances of assembled full cells. Reproduced with permission from Ref. [131]. Copyright 2021, American Chemical Society.

tion of Mn with Ni led to a decreased capacity, but improved its cycling stability and electrochemical performance. Therefore, if the ratio of the constituent elements (mainly Ni and Mn) of these Li- and Mn-rich layered compounds are adjusted, it is beneficial to improve their cycling stability and electrochemical performance. In this regard, the strategy used two lithium-rich cathodes ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.27}\text{Mn}_{0.40}\text{Co}_{0.13}\text{O}_2$) with different nickel contents in a full cell with graphite as the anode to improve its cycling stability and its electrochemical performance.^[132] The full cell with $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ as the cathode initially exhibits a high capacity of about 250 mAh g⁻¹, decaying to 130 mAh g⁻¹ after 120 cycles. Comparing the electrochemical performance of the full cell consisting of $\text{Li}_{1.2}\text{Ni}_{0.27}\text{Mn}_{0.40}\text{Co}_{0.13}\text{O}_2$ as the cathode material, the full cell exhibited about 190 mAh g⁻¹ capacity and stable cycle life. The experiments illustrate the cycle stability, energy density, and electrochemical performance of LIBs with properly tuned Ni and Mn over-lithiated cathode materials. The direct use of over-lithiated cathode materials is an effective strategy, and the process is simple. However, too high a voltage can adversely affect the stability of the electrolyte and may create safety problems.

The use of over-lithiated cathode materials, which have a high specific energy, can increase the energy density of LIBs. Additionally, the additional lithium source compensates for irreversible lithium loss, reduces structural changes in the cathode material during charging and discharging, and improves cycling stability. However, over-lithiation of the cathode material can increase the safety risk of the battery. Excessive lithium may lead to internal short-circuiting or the generation of lithium dendrites, which can increase the manufacturing cost of the battery. Therefore, it is reasonable to optimize the degree of over-lithiation to control the lithium content and reduce the safety risk. Simultaneously, enhance the preparation process of

over-lithiated cathode material to improve its purity and stability.

4. Other Pre-Lithiation Strategies

In addition to the most studied pre-lithiation at the electrode level, there is also pre-lithiation of other components in LIBs that equally complement the active lithium loss. This section is divided into three main categories: electrolyte pre-lithiation, separator pre-lithiation and binder pre-lithiation, respectively.

4.1. Electrolyte Pre-Lithiation

Electrolyte pre-lithiation is a technique that releases active lithium by electrolysis of electrolyte salts. This is done prior to the initial charging of the battery to compensate for irreversible lithium loss and improve the ICE. The process of electrolyte pre-lithiation has similar advantages to electrochemical pre-lithiation. It can be achieved by selecting appropriate electrolyte salts and controlling the conditions of the electrolysis. The use of cheap lithium salts or sacrificial electrodes instead of lithium metal can reduce costs and safety risks. Furthermore, electrolyte salts are typically stable enough to replenish lithium during electrolysis without undergoing decomposition or side reactions. For example, lithium chloride (LiCl) is widely used in electrolytes as a low-cost electrolyte salt that forms gaseous chloride upon oxidation of chloride ions. A research has formed protective a SEI layer on Si films based on LiCl electrolytes using boron-containing additives and CO₂.^[133,134] CO₂ has been reported as an effective additive and solubility enhancer to optimize pre-lithiated electrolytes based on γ -butyrolactone and LiCl (Figure 12a, b). Reversible lithiation experiments on Si//

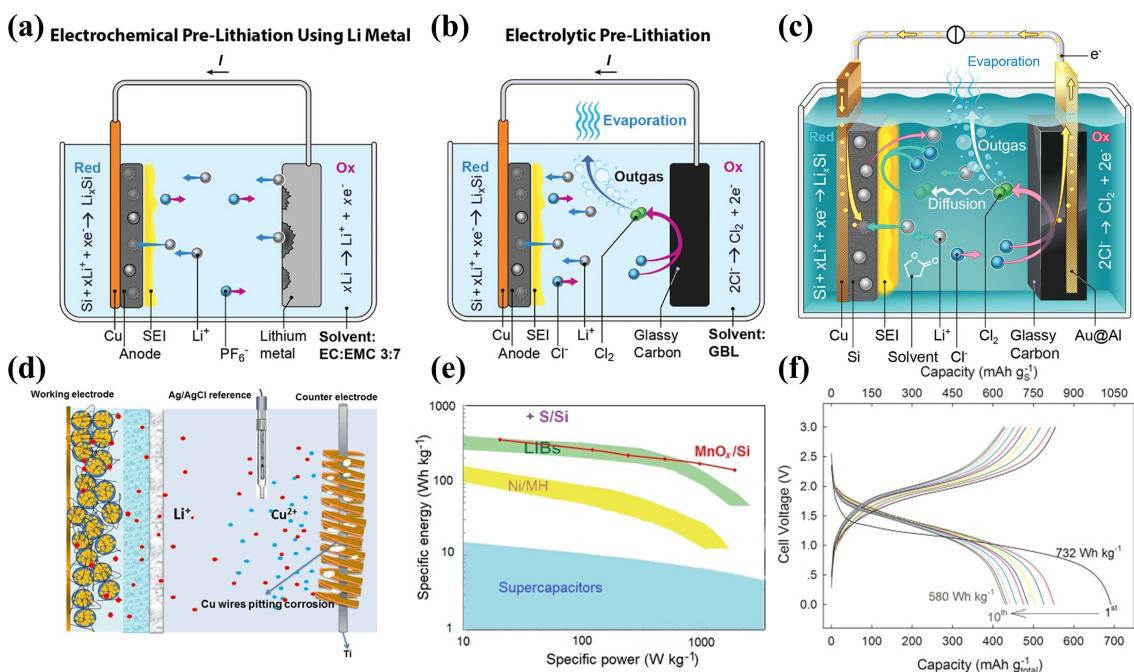


Figure 12. (a) Electrolytic pre-lithiation based on the oxidation of the electrolyte salt anions. (b) Schematic illustration of the Cl_2/Cl^- shuttle mechanism. (c) Principle of the pre-lithiation of the Si electrode. (d) Ragone plot of the MnO_x/Si and S/Si full cells. Reproduced with permission from Ref. [133]. Copyright 2022, Wiley-VCH. (e) Charge and discharge curves. Reproduced with permission from Ref. [135]. Copyright 2015, Wiley-VCH.

Li metal cell demonstrated that the optimized electrolyte was equivalent to $1 \text{ M LiPF}_6/\text{EC:EMC}=3:7$ with a Coulomb efficiency of 95–96%.

In order to add Li ions to the electrolyte, a new lithium metal-free electrolytic cell is used to achieve pre-lithiation with a binderless silicon electrode using Cu as the sacrificial anode, a $0.5 \text{ M Li}_2\text{SO}_4$ -based aqueous electrolyte with a cathode containing an organic carbonate electrolyte half of the electrolyte, and an organic carbonate electrolyte. The cells are separated by lithium superionic conductor films ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$). In addition, a new electrolytic cell in which silicon electrodes can be pre-lithiated in a lithium-containing aqueous solution in a well-controlled manner in a lithium metal-free manner. MnO_x/Si and S/Si Li ion batteries were assembled using pre-lithiated Si anodes, and high specific energies of 349 and 732 Wh kg^{-1} were obtained, respectively. (Figure 12c, d, e).^[135] This is the first report of a full cell without using The entire process of fabricating full cells with two lithium-deficient electrodes without using lithium metal as a lithium source is reported for the initial time.

Electrolyte pre-lithiation compensates for irreversible lithium loss by providing a homogeneous lithium source, improving ICE and cycle stability. However, excessive electrolyte consumption during electrolyte pre-lithiation may reduce battery life due to the lack of certain safety protections, and the lithium source adds additional cost. To reduce the risk during pre-lithiation and supplement the lithium source, it is important to screen suitable lithium-rich electrolyte materials, optimize the lithium content of the pre-lithiation process, and control the appropriate degree of pre-lithiation.

4.2. Separator Pre-Lithiation

The separator plays a crucial role in preventing short circuits within the battery structure. To achieve this, separator pre-lithiation is employed by introducing lithium-containing compounds onto the separator. These compounds react with the lithium ions in the electrolyte during charging and discharging, generating lithium metal and releasing electrons. This process effectively compensates for the loss of active lithium. The separator pre-lithiation method offers the advantage of enhancing the ICE of the battery without changing the cathode and anode materials, while avoiding the formation of lithium dendrites, thereby improving the safety of the battery.^[136,137] Pre-lithiation of the separator can effectively compensate for the active lithium loss. Recently, a functional separator pre-lithiation, in which fluorite-resistant (LFO) was supported as a pre-lithiation agent on the separator, so that a conventional LIBs separator made of laminated polypropylene/polyethylene layers was modified by a functional agent or radical.^[138] The LFO-supported separator enables a functional separator that rapidly detects and responds to early dendrite formation (Figure 13a). This method of pre-lithiation of the separator avoids the introduction of high alkalinity into the cathode, reduces the potential of gelation of the cathode active material thereby protecting the cathode from damage, and improves the (electro)chemical stability of the electrode/electrolyte (Figure 13b). The experimental results show that the reversible capacity of the full cell is increased by 40% and the specific energy of the 3 Ah pouch cell is stabilized at 330 Wh kg^{-1} . Moreover, this functional separator pre-lithium is compatible with the existing LIBs production process and has no adverse

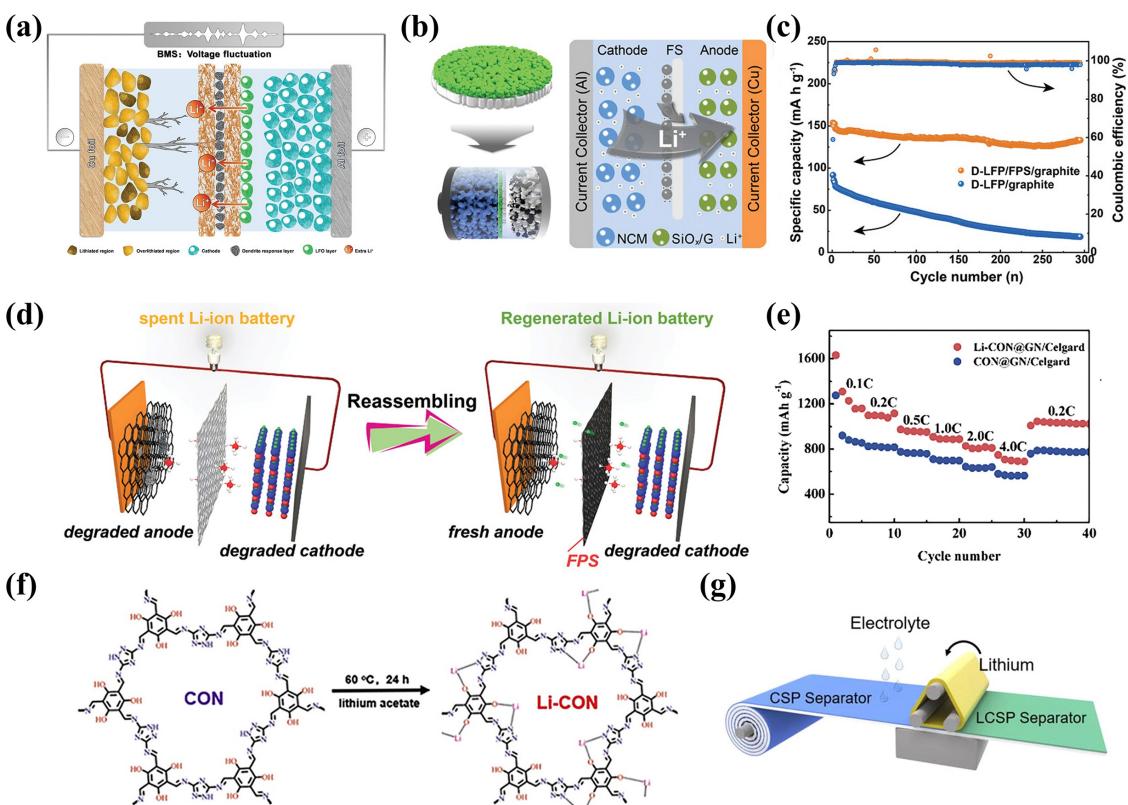


Figure 13. (a) The separator combining the LFO pre-lithiation layer. (b) Schematic diagram showing the typical FSP process. Reproduced with permission from Ref. [138]. Copyright 2023, Wiley-VCH. (c) Comparison of the cycling stability for the regenerated cell with and without FPS. (d) Schematic illustration of the direct regeneration strategy based on FPS. Reproduced with permission from Ref. [139]. Copyright 2022, Wiley-VCH. (e) Rate performance, and (f) the synthesis scheme of the Li-CON. Reproduced with permission from Ref. [140]. Copyright 2020, Elsevier. (g) Schematic illustration for the scalable fabrication process of the LCSP separator. Reproduced with permission from Ref.[141]. Copyright 2021, American Chemical Society.

effect on battery formation and operation. At lower discharge cut-off voltages, the separator can recover part of the inserted lithium capacity and prevent the formation of dendrites in case of localized over-lithiation. Additional efforts in this area will help create high-energy rechargeable LIBs.

With the strategy of directly transferring Li ions to the anode during charging via a pre-lithiated separator, a study has been conducted through utilized an in-situ electrochemical process via a pre-lithiated separator (FPS) to directly recycle lithium iron phosphate cathodes (LFPs).^[139] Compared to existing recycling strategies, this method utilizes a pre-lithiated separator to fully utilize degraded cathode waste without destroying the original structure, significantly reducing the cost of remanufacturing cathode electrodes through pre-lithiation technology alone. This new separator FPS storage releases active Li and is prepared by coating a commercial separator with a thin layer of lithium-rich material ($\text{Li}_2\text{C}_2\text{O}_4$). Degraded LFP electrodes were directly reassembled with FPS separators and fresh graphite anodes to form a regenerative battery (Figure 13c, d). It showed that the irreversible electrochemical decomposition of $\text{Li}_2\text{C}_2\text{O}_4$ on FPS provided additional Li ions to compensate for the lithium-deficient LFP cathode during the initial cycle, the regenerated LIBs exhibited excellent electrochemical performance and the replacement of commercial

separator with FPS showed good compatibility with the existing battery fitting process.

The method of binder pre-lithiation has also been used in many reports, a two-dimensional lithiated covalent organic framework nanosheet (Li-CON) layer with organized lithiation sites. These lithiation sites significantly facilitated Li ions transport, and Li-CON also promoted lower reactivation energy fracture of Li–S bonds, leading to fast polysulfide conversion kinetics.^[140] As a result, the Li-CON-modified separator possesses high lithium ion conductivity and transfer number, while inhibiting polysulfide shuttling and lowering the charging overpotential, with excellent long-cycle and high-multiplier performance (Figure 13e, f). Herein, a pre-lithiation separator by modifying a commercial separator with a $\text{Li}_2\text{S}/\text{Co}$ nanocomposite to compensate for the initial capacity loss is proposed by Rao' group.^[141] The experiments applied $\text{CoS}_2/\text{Co}_3\text{S}_4$ on commercial polypropylene separator (CSP separator) to form precursor separator, after which the precursor separator was directly contacted with lithium metal and thus reacted (Figure 13g), resulting in the formation of lithium-containing $\text{Li}_2\text{S}/\text{Co}$ as a lithium-compatible pre-lithiated separator (LCSP). The lithium capacity of the LCSP separator was as high as 993 mAh g^{-1} and the $\text{LiFePO}_4/\text{Gr}$ full cell also showed good cycle performance.

Separator pre-lithiation reduces the lithium demand inside the battery and improves the energy density of LIBs. Addition-

ally, separator pre-lithiation can decrease lithium loss in the active material of the cathode and anode, mitigating volume expansion and improving their cycling performance. However, there are currently two main drawbacks: the uniformity of the separator pre-lithiation coating and the control of its thickness. These issues may lead to inconsistent battery performance, increased manufacturing costs, and process complexity. Improving the pre-lithiation separator process to maintain consistent coating thickness and uniformity is crucial. Specific reagents can be added to the separator pre-lithiation coating to enhance the battery's electrochemical performance.

4.3. Binder Pre-Lithiation

Electrode binders are crucial in attaching active substances and conductive additives to the current collector. This process has a significant impact on the electrode's electrochemical performance during charging and discharging. The pre-lithiation binder is a lithium-containing polymer or inorganic compound. It is introduced into the electrode material during pre-lithiation lithium replenishment to compensate for the loss of active lithium. This is achieved by generating lithium metal and releasing electrons through its interaction with the active substance and the electrolyte.^[142–144] Binders pre-lithiation makes use of the fact that some of the protons in certain carboxylate groups ($-\text{COOH}$, $-\text{OH}$) in the anode binders could be replaced by Li ions, thus allowing lithium to be replenished to the anode in advance, making up for the ICL. Water-based

binders with hydroxyl or carboxyl groups (alginate, carboxymethyl cellulose (CMC)), and polyacrylic acid (PAA)) are generally chosen as their binders for silicon-based anodes precisely as their functional groups may contribute to the formation of strong covalent bonding with silanol radicals on the surface of Si (SiOH), which can inhibit a certain volume change.^[145,146] Considering this characteristic, a binder pre-lithiation strategy was proposed for the Si electrode. The hard/soft modulated trifunctional network bond (N-P-LiPN) is constructed by hydrogen bonding effect using partially lithiated poly (acrylic acid) (P-LiPAA) as the backbone and partially lithiated naphthoic acid (P-LiNF) as the buffer (Figure 14a).^[147] N-P-LiPN has a strong physical adhesion and is not affected by the volume expansion of the silicon anode. In addition, Li ions can be rapidly transferred through the N-P-LiPN, which effectively improves the conductive ionic properties of silicon anodes. Thanks to these advantages, the half-cell shows a maximum ICE of 93.18% and an excellent cycle performance. (Figure 14b, c).

Accordingly, Hu *et al.*^[148] investigated the effect of pre-lithiated PAA binder in solution and slurry, and the experiments were carried out using LiOH for pre-lithiation of PAA bond pairs by titration to pH~7. The performance of Si/Gr composite electrodes prepared using the binders as well as the electrochemical cycling performance were characterized (Figure 14d). It was found that pre-lithiation increased the viscosity of PAA by a factor of ten at low shear rates, and at high shear rates, the slurry is uniformly mixed and stirred without any increase in viscosity. However, the pre-lithiated PAA binder also

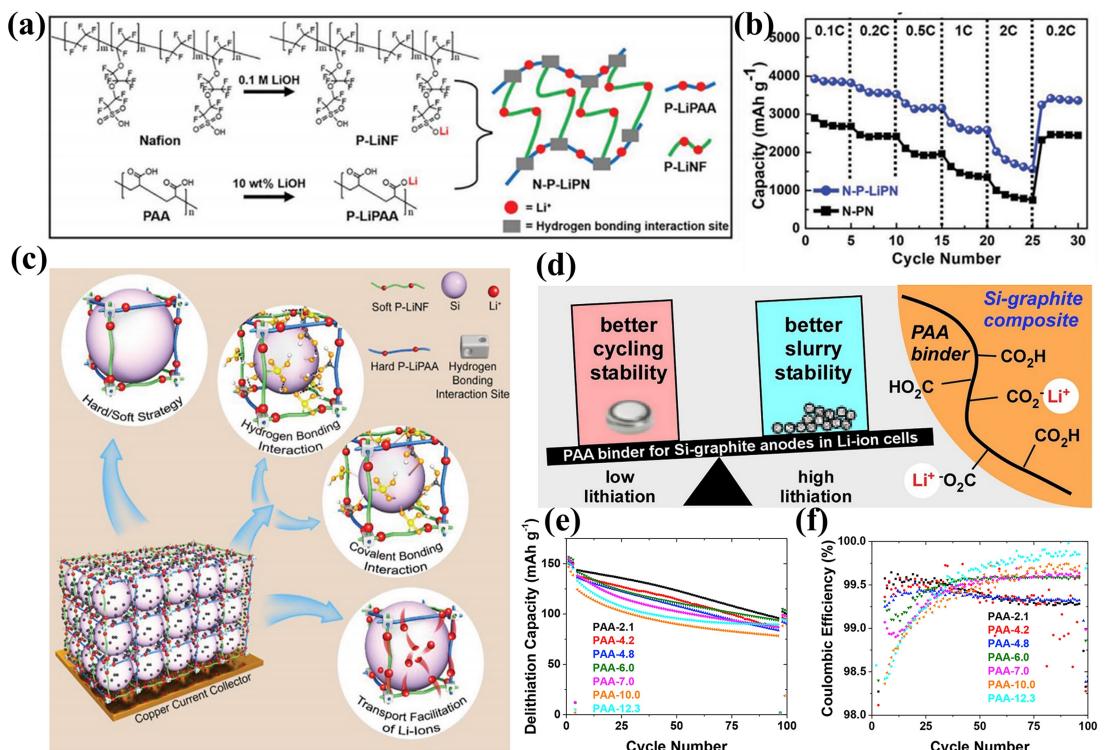


Figure 14. (a) Schematic of the preparation of the N-P-LiPN binder. (b) Rate performances, and (c) schematic illustration of N-P-LiPN binder in the Si electrode. Reproduced with permission from Ref. [147]. Copyright 2020, Wiley-VCH. (d) Schematic diagram of pre-lithiation process of PAA binder. (e) Specific discharge-capacity and (f) CE of assembled full cells. Reproduced with permission from Ref. [148]. Copyright 2019, Elsevier.

eroded the Si particles, resulting in poor cycling performance of the half-cells and full-cells (Figure 14e, f).

To solve this problem, the use of pre-lithiation of poly(acrylic acid) binder (Li_xPAA) to obtain an interwoven composite binder that enables stable cyclability of highly loaded SiO_x and Si nanoparticle electrodes, and improves the ICE of the Si-based anode mainly by precisely controlling the degree of pre-lithiation of the PAA binder (Figure 15a). The electrochemical performance of the Si-based anode by the Li_xPAA binder was significantly improved by the polymer chain conformation.^[149] The significant improvement is attributed to the change in polymer chain conformation and the generation of a large number of $-\text{COOLi}$ groups. The change in polymer chain conformation from coiled to stretched leads to enhanced bond strength and improved mechanical properties of the binder. The large amount of $-\text{COOLi}$ generation alleviated the side reactions of the binder, provided an extra source of lithium, and enhanced the Li transport kinetics of the binder. The ICE of the highly loaded SiO_x anode was found to increase by 10.9% when $\text{Li}_{0.75}\text{PAA}$ replaced the PAA binder, with 70% ICE after 170 cycles with $\text{SiO}_x@\text{Li}_{0.75}\text{PAA}$ anode at 0.2 C and 90% ICE after 80 cycles with $\text{Si}@\text{Li}_{0.75}\text{PAA}$ anode at 0.1 C (Figure 15b).

However, since the reaction between the Si-based anode and lithium is an exothermic process, the volume change during charging and discharging makes the high temperature binder a requirement, and water-soluble high temperature binders are compatible with current Si-based anode fabrication processes. Therefore, a water-soluble lithium-substituted polyamide acid-based binder (Li-Pa) is proposed by Zhu's group, which can withstand the high temperatures of pre-lithiation and efficiently bond the active materials together, providing water-solubility and mechanical dexterity (Figure 15c). The

results were found to provide 87% capacity retention after 50 cycles in half-cells with Li-Pa binder, and a full-cell initial discharge capacity of 2.83 mAh g^{-2} with an ICE of 83.5% (Figure 15d). This pre-lithiated binder holds promise as an alternative to conventional PAA and polyvinylidene fluoride (PVDF) to facilitate large-scale manufacturing of commercial LIBs with high energy density.^[150] Based on the need for an in-depth understanding of how polymer materials affect the behavior of the electrode/electrolyte interface, a strategy has proposed a simple and effective surface coating method for high-pressure composite cathodes.^[151] The LiPAA surface coating was integrated into $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ on a lithium-rich cathode using the solution casting method. The specific charge of the battery was significantly improved from about 20 mAh g^{-1} at the initial cycle to as high as 50 mAh g^{-1} at the 100th cycle, while the capacity retention of the battery was also enhanced. In addition, reduced CO_2 release was detected from the coated electrodes in the electrochemical mass spectrometry analysis, suggesting that the LiPAA interrupts the electrolyte decomposition reaction and enhances the stability of the electrodes interface at high potentials. This Li-rich polymer coating creates a stable artificial interface with the anode, facilitating long battery cycles and properly inhibiting electrolyte decomposition.

The pre-lithiation binder can store a sufficient amount of Li ions, which directly affects the electrode structure and performance. It also stabilizes the electrode structure, increases the electrochemical reaction area, and improves the energy density of the battery. Pre-lithiation of the binder can improve the interfacial reaction between the binder, active substance, and electrolyte, which can prevent side reactions and improve the characterization of interfacial questions. This method offers a

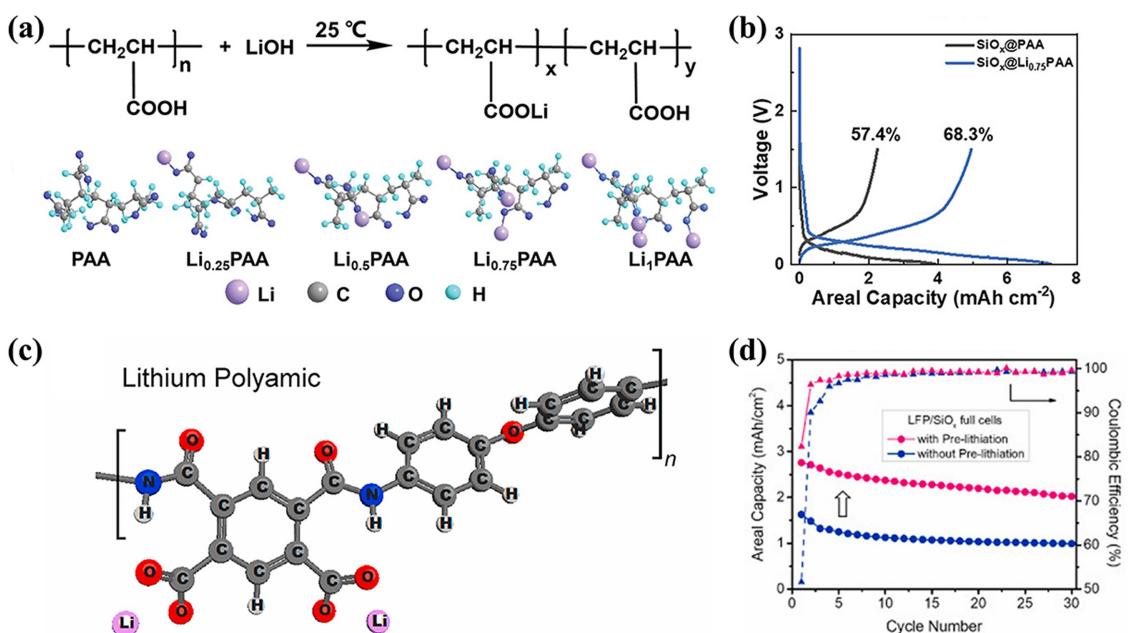


Figure 15. (a) Synthesis scheme and chemical structure of the Li_xPAA binders, and (b) their initial charge-discharge curves. Reproduced with permission from Ref. [149]. Copyright 2022, Wiley-VCH. (c) Schematic diagram of the optimized molecular structures for Li-Pa. (d) Cycling performance of assembled SiO_x/LFP full cells. Reproduced with permission from Ref. [150]. Copyright 2021, Elsevier.

simpler battery manufacturing process compared to other pre-lithiation techniques. However, it is important to note that not all binders are compatible with the electrode structure, which may result in structural differences. Furthermore, the uniformity of the pre-lithiation binder may pose safety hazards. To enhance the practicality of pre-lithiation binders, it is essential to develop a new type of bond with stable chemical properties that are compatible with both the electrode and electrolyte for pre-lithiation. Additionally, adjusting certain parameters in the pre-lithiation process can promote uniform and efficient pre-lithiation.

5. Summary and Outlook

As a promising electrochemical energy storage technology for renewable energy, LIBs have received extensive research and attention in the field of large-scale energy storage in recent years. However, during the initial charging and discharging process, part of the active lithium is irreversibly depleted to form a SEI layer on the anode surface, resulting in a lower ICE and limited cycle life. To this end, as an effective strategy, pre-lithiation is proposed and utilized to compensate for the ICL by adding active lithium before the fabrication of LIBs systems, leading to improved energy density and cycle stability. For this, increasingly more researchers have investigated various pre-lithiation methods to compensate the lithium loss and improve the ICE recently.

In this review, the internal reasons for the initial ICL of LIBs are analyzed, and various pre-lithiation techniques based on different components of LIBs are summarized and discussed, including the anode pre-lithiation strategy, cathode pre-lithiation strategy, and other pre-lithiation strategy. Despite the fruitful progress of the above studies, the understanding of the pre-lithiation techniques for LIBs based on the existing studies and findings is far from adequate due to the various pre-lithiation techniques having certain flaws and shortcomings. Therefore, there is a need for a deeper study and attention should also be paid to the deficiencies of the various methods of pre-lithiation strategies for LIBs to achieve a more comprehensive and holistic understanding. Here, we give some summaries and outlooks of current pre-lithiation technologies.

Firstly, for anode pre-lithiation additives, it is necessary to have not only a high theoretical Li ions capacity but also a low lithium extraction capacity. The entire pre-lithiation process is driven by the potential difference between the additive and the anode material, thus compensating for the irreversible lithium loss. However, it is critical to address the air stability of these additives, mainly because of the large contact area between the active metal and the air, which can lead to safety hazards. The electrochemical pre-lithiation process is mainly controlled by the contact time and the applied voltage. However, there is a certain complexity to the experimental procedure. Moreover, the anode materials after electrochemical pre-lithiation are chemically more reactive and cannot be stably stored in air. The realization of the chemical pre-lithiation process is mainly to design a kind of pre-lithiation reagent with low redox potential,

and transfer Li ions by controlling the concentration and time of the solution to soak the anode. However, the pre-lithiation solution is generally an organic solvent, which is poorly air-stable and toxic, and needs to be operated in an inert atmosphere, making it difficult to commercialize. Therefore, it is necessary to develop anode additives with excellent air stability, optimize the electrochemical pre-lithiation process, and find a pre-lithiation reagent with good air stability and sufficiently low redox potential for practical application.

Secondly, cathode pre-lithiation is an effective strategy to improve the electrochemical performance of LIBs by replenishing Li ions to the cathode using cathode additives and over-lithiated cathode materials. The migration of Li ions is mainly transferred to the anode side through the cathode to form the SEI layer, and the additives are generally selected as Li-rich compounds, which are required to have a strong ability to give Li ions. The direct use of over-lithiated cathode materials as the cathode of LIBs is equivalent to directly providing an additional lithium source to compensate for the loss of active lithium, which improves the cycle life of LIBs. However, cathode additives decompose to produce N₂ and O₂ during the cycling process of the batteries, and excessive voltage when using over-lithiated cathode materials reduces the stability of the electrolyte and creates a safety hazard. Therefore, it is necessary to explore additives and cathode materials with high irreversible capacity and suitable decomposition potential to compensate for the loss of active lithium.

Thirdly, in addition to the direct complement of active lithium to both the anode and cathode, lithium sources can be appropriately complemented in other structures of the batteries. Such as using electrolytic electrolyte salt to precipitate Li ions, coating a thin layer of lithium-rich material on the cathode side of the separator and exchanging lithium atoms with some of the protons in the binder groups. Pre-lithiation can be achieved rapidly using lithium salts or sacrificial electrodes as electrolyte salt reactions. Providing a lithium source on the cathode side of the separator for pre-lithiation has become a battery recycling strategy that does not disrupt the original electrode structure and contributes to safe and sustainable rechargeable batteries. Some binders with hydroxyl or carboxyl groups can be utilized to achieve pre-lithiation by reacting with the lithium source, which improves the electrochemical performance of LIBs. However, there are still some limitations of this pre-lithiation strategy, such as the high cost of lithium salts, the poor air stability of lithium-rich materials, and the short chain length of some oily binders that are not easy to be replaced by lithium atoms, which have to be solved to realize the successful pre-lithiation of LIBs.

Although a variety of pre-lithiation strategies have been reported, there are still a lot of problems to be considered in the actual commercial applications. The following aspects cover some of the problems and issues to be considered in the current research and provide references for future pre-lithiation work. (1) Developing pre-lithiation reagents and additives with significant pre-lithiation effect and safety and stability: choosing a suitable pre-lithiation reagent or additive can significantly improve the electrochemical performance and energy density

of LIBs, while paying attention to the reactivity, toxicity and hazardousness of some chemicals and methods, which require special preparation and safety measures. (2) Control the degree of pre-lithiation: considering the safety and aging behavior of the battery, the degree of pre-lithiation needs to be precisely controlled, because excessive lithium replenishment will also lead to the generation of lithium dendrites to puncture the separator, triggering safety hazards. (3) Improve the compatibility of pre-lithiation and battery process: many pre-lithiation of active materials or pre-lithiation reagents are unstable under ambient air conditions. (4) Minimize the cost of pre-lithiation: if the cost of pre-lithiation methods or additives is too high it will lose its advantage, so the pre-lithiation process should be as low-cost as possible. (5) Pre-lithiation for different types of anodes also affects the cycle life; a slight excess of lithium is beneficial to the cycling performance of carbon-based anodes, and when pre-lithiation is performed for alloy-conversion and composite anodes, which have large volume changes, the amount of pre-lithiation, the N/P ratio, and the modulation of the interfacial SEI layer are very important for the effect on the cycling stability of the full cell.

In conclusion, pre-lithiation technology supplements the initial irreversible loss of active lithium, which is an indispensable and important step in battery manufacturing. Therefore, a comprehensive in-depth understanding of the pre-lithiation technology of LIBs is undoubtedly an important guide to increasing their energy density and cycle life. Significantly, the mature pre-lithiation strategy promotes the practical application of LIBs, for this purpose, we provide an overview of the advantages and challenges of various pre-lithiation methods and present a specific outlook on each pre-lithiation strategy. In view of the pre-lithiation technology is an important part of practical commercial production of high-energy batteries, this review provides guidance not only for the pre-lithiation of LIBs, but also for pre-sodiation of sodium-ion batteries or other pre-treatment strategies for alternative battery technologies.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: lithium-ion batteries · pre-lithiation technology · irreversible capacity loss · solid electrolyte interface · Coulombic efficiency

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