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Promises and Challenges of the Practical Implementation of Prelithiation in Lithium-Ion Batteries

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Lithium-ion batteries (LIBs) have changed lives since their invention in the early 1990s. Further improvement of their energy density is highly desirable to meet the increasing demands of energy storage applications. Active lithium loss in the initial charge process appreciably reduces the capacity and energy density of LIBs due to the formation of a solid electrolyte interface (SEI) on the anode surface, especially for Si based anodes in high-energy-density batteries. To solve this issue, prelithiation to provide additional active lithium into the battery has been widely accepted as one of the most promising strategies. Here, key parameters/issues for the practical implementation of prelithiation approaches in LIBs are discussed, including donable lithium-ion capacity/prelithiation efficiency, chemical and ambient stability of the prelithiation materials/reagents, safety hazards of prelithiation, residues and side reactions during prelithiation, potential effect on electrochemical performance, industrial compatibility, and scalability of the prelithiation, many of which are often overlooked in academic literature. Moreover, insights are offered regarding the potential future directions in the development of this burgeoning field. Continuous progress in prelithiation is essential and urgent to enable next-generation high-energy-density LIBs in the near future.

1. Introduction

Lithium-ion batteries (LIBs) have been dominating in portable electronics and electric vehicles and are becoming the leading technology for grid energy storage.[1–5] Energy density is one main property of LIBs, and it has been driving the entire battery technology forward to meet the ever increasing energy demands of the modern society.[6–9] For the existing LIBs with graphite-based anodes, active lithium from the lithium-containing oxide or phosphate cathode is consumed due to the side reactions during the formation of solid electrolyte interface (SEI) on the anode surface, accompanied by the decomposition of liquid electrolyte. This leads to Coulombic efficiency values lower than 100% in the very initial charge/discharge cycles (e.g., 90%–95% for the first cycle), which appreciably reduces the energy density of LIBs.[10–13] For the next-generation high-energy-density LIBs, high-capacity anodes (e.g., Si, Sn, and P with alloy reaction mechanism) undergo much more serious side reactions and show much more initial lithium loss (e.g., >15%) than the graphite-based anodes. Moreover, the side reactions of these high-capacity anodes continue to take place for several cycles, sometimes even tens of cycles, before the stabilization of Coulombic efficiency to over 99.9%, due to the large volume change of these materials (e.g., $\approx$420% for Si, $\approx$260% for Sn, and $\approx$300% for P) from lithium-free state to full lithiation state, which leads to large amount of accumulated lithium loss.[14,15] Consequently, the usable lithium-ion capacity and overall energy density of LIBs using these high-capacity anode materials would be significantly decreased.

Prelithiation has been widely investigated as a promising strategy to resolve this lithium loss issue and increase the energy density of LIBs. With the specific purpose of compensating for the initial lithium loss in LIBs, prelithiation is conceptually independent from the pretreatment of battery materials or electrodes, and it can be simply regarded as providing additional active lithium using specific prelithiation reagents/materials or processing to LIBs prior to battery cell cycling. To increase active lithium inside the entire LIBs, prelithiation can be performed on different battery components, cathodes, or anodes, and also at different levels, materials, or electrodes, depending on the prelithiation approaches. Till now, various prelithiation methods have been developed, including electrochemical prelithiation at the electrode level,[16–19] chemical prelithiation at the materials or electrode level,[20–22] prelithiation additives for cathodes and anodes,[8,23–27] and direct contact/short circuit between a negative electrode and a lithium metal foil.[28–31] These prelithiation methods with various mechanisms show different prelithiation efficiency or capability in increasing the energy density of LIBs and other effects, and

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also face different challenges/issues for practical applications. Various materials/reagents are used and different processing equipment/conditions are required for different prelithiation methods, which lead to different challenges for their practical applications in battery industry across multiple length scales. Previous review articles about prelithiation for LIBs are organized by individual prelithiation methods.[32–36] We believe that different prelithiation methods share some common parameters that have to be achieved and common challenges/issues that have to be solved for practical application. Here we organize our Perspective based on the key parameters of prelithiation as well as the challenges/issues associated with prelithiation itself, instead of examining individual prelithiation method separately, which include: donable lithium-ion capacity/prelithiation efficiency, chemical and ambient stability of the prelithiation materials/reagents, safety hazards of prelithiation, residues and side reactions during prelithiation (e.g., gas evolution), potential effect on electrochemical performance (e.g., inert materials/residuals introduced by prelithiation), and industrial compatibility and scalability of the prelithiation. Yet the scientific literature mainly discusses materials design/processing toward apparently excellent electrochemical performance. Many of important parameters are often overlooked, which are critical for practical applicability in battery industry. Also, in this Perspective, typical examples of these important parameters/issues are illustrated. Moreover, we offer insights regarding the rational design of materials/reagents and processing to solve these issues simultaneously and realize successful prelithiation for possible industrial applications.

2. Materials, Key Parameters, and Processing of Prelithiation

Active lithium can be involved into LIBs at materials level, or electrode level using different prelithiation methods (as shown in **Figure 1**). Materials/reagents with high active Li content can be used as prelithiation additives directly integrated into electrodes (cathodes or anodes) during slurry mixing. Stabilized lithium metal powders (SLMPs) and lithium silicide (e.g., $Li_{15}Si_4$) particles are two typical anode prelithiation additives that possess high theoretical lithium-ion capacities and low lithium extraction potential. For lithium compensation at the cathode side, lithium nitride (e.g., Li_3N)[27] powders and metal/Li_2O nanocomposites[8] can contribute high donable lithium-ion capacities below the charge cut-off potential window of the existing cathodes.

To fabricate these prelithiation additives with high lithium-ion capacities, metallic Li is often used as the raw material. Typically, SLMPs are synthesized using high-speed mechanical stirring of molten metallic Li, accompanied by surface passivation process to form a Li_2CO_3 nanoshell. Si particles can react with molten metallic Li through alloy reaction to produce $Li_{15}Si_4$ under mechanical stirring in Ar atmosphere. Utilizing chemical conversion reaction, LiF/Co nanocomposites can be fabricated through the reaction between molten metallic Li and FeF_3.[37] Si-based anodes can be lithiated by solutions of Li-biphenyl (Li-Bp) derivatives due to their low chemical potential (e.g., <0.2 V vs Li^+/Li) to generate the corresponding lithiation states. At the cathode side, lithium-rich $Li_{1+x}Ni_{0.65}Mn_{0.20}Co_{0.15}O_2$ can be realized using similar approach of chemical (over)lithiation through the reaction between Li-naphthalene (Li-Naph) solution and commercial $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$.[38] It is noted that some prelithiation additives are reactive with polar solvents (such as *N*-methyl-2-pyrrolidone, NMP) and moisture in the environment, and are incompatible with the existing slurry fabrication processing. To utilize the high-capacity SLMPs for anode prelithiation additives, direct calendering of dry powders or dropping their suspensions in low polarity solvents onto electrodes have shown success in lab scale. To be compatible with the existing battery industry, prelithiation additives should be integrated into electrode using slurry mixing, electrode casting, and drying processes. In this respect, cathode prelithiation additives are more promising due to their lower reactivity. Metal/LiF/Li_2O nanocomposites were successfully introduced into $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode using slurry approach in ambient condition with low humidity (<20%).[39]

Prelithiation at electrode level is an alternative approach, with numerous successful examples in lab scale. Through the configuration of Li metal half-cell with an external circuit, the lithiation degree can be controlled accurately. Short-circuit contact between electrode and Li foil in the presence of electrolyte provides another choice, which does not involve cell assembling/disassembling processes. During the processing, applied external pressure helps to realize uniform electrochemical lithiation reaction. It is noted that chemical prelithiation is universal for both materials level and electrode level. By direct immersion of prefabricated electrode into Li-arene solutions, uniform lithiation can be achieved. The prelithiation approaches at electrode level can avoid the slurry processing, providing more opportunities for the practical application of sensitive prelithiation materials. Successful chemical prelithiation at both cathode and anode sides was realized, including lithium-rich $Li_{1+x}Ni_{0.65}Mn_{0.20}Co_{0.15}O_2$ for cathode[38] and Li_xSi for anode. Impressively, with high overall capacities (e.g., >700 mAh g^{-1} based on the mass of sulfurized polyacrylonitrile, SPAN), electrode of SPAN was fully lithiated into Li_2S-PAN through its reaction with Li-Naph solution.[40] Also, chemical prelithiation can also be realized using direct solid chemical reaction between Li foil and certain specific metal foil electrode such as Sn foil.[41]

It should be noted that prelithiation involves various reagents/materials and operations, which cause additional requirements in comparison to the regular battery processing. Several important parameters, which are critical for practical applicability in battery industry, include donable lithium-ion capacity/prelithiation efficiency, chemical and ambient stability of the prelithiation materials/reagents, safety hazards of prelithiation, residues and side reactions during prelithiation (e.g., gas evolution), potential effect on electrochemical performance (e.g., inert materials/residuals introduced by prelithiation), and industrial compatibility and scalability of the prelithiation. In the sections below, these important parameters/issues will be analyzed in detail, with typical examples and future directions illustrated.

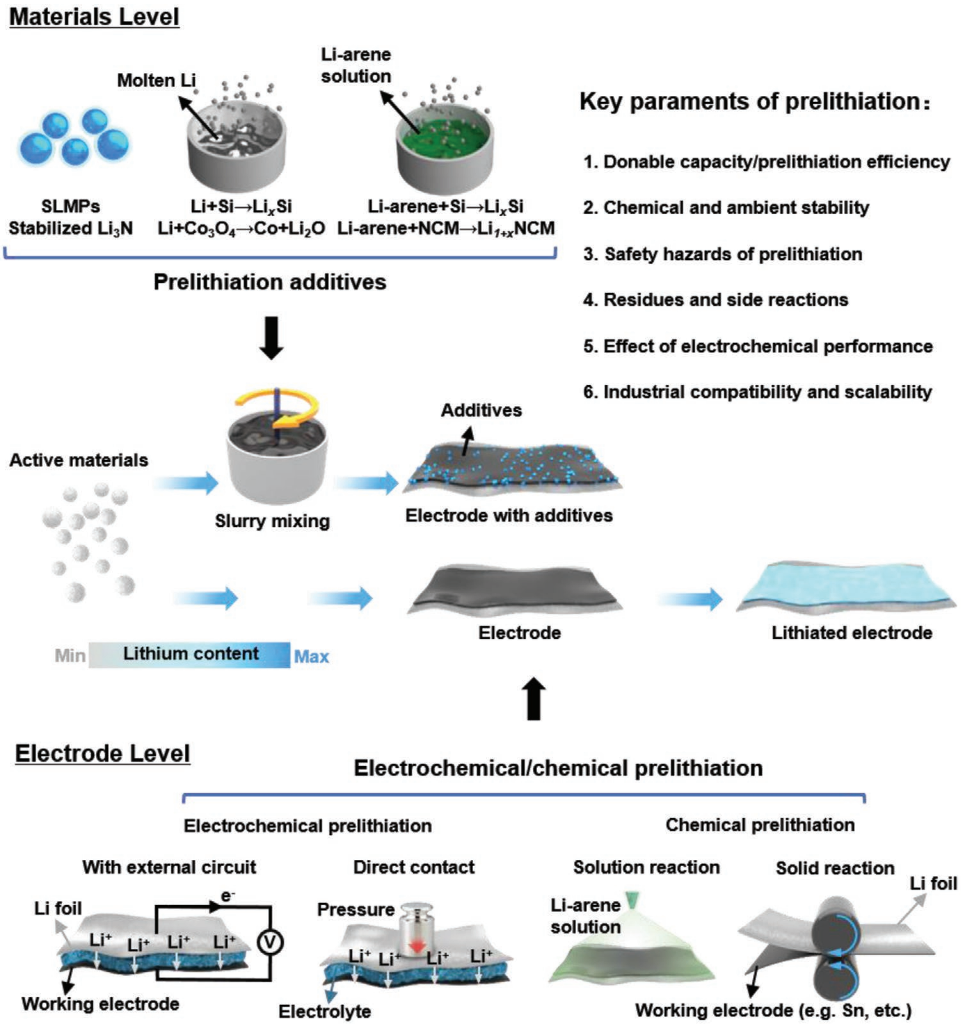

Figure 1. Materials, methods, and key parameters of battery prelithiation. Prelithiation has been illustrated at both materials level and electrode level, including fabrication and application of prelithiation materials, electrochemical prelithiation, and chemical prelithiation at electrode level. Key parameters of prelithiation have been listed, depending on various prelithiation materials and processing.

3. Donable Lithium-Ion Capacity/Prelithiation Efficiency

High-capacity anode materials (e.g., Si, Sn, and P with alloy reaction mechanism) usually undergo serious side reactions and show high initial lithium loss (e.g., >15%) in the initial cycle. This issue even gets worse when nanomaterials with higher specific area are applied, necessitating high-efficiency lithium compensation. Donable lithium-ion capacity or prelithiation efficiency is a fundamental parameter of prelithiation, which decides the increased capacity and energy density of LIBs that prelithiation can help to realize. The higher the lithium-ion capacity that the prelithiation reagent/material provides, the lesser the amount of prelithiation reagent/material is required for lithium compensation.

Chemical prelithiation is a simple and efficient method performed on anode utilizing Li-arene solutions as prelithiation reagents for direct lithiation of active materials at materials or electrode level. Li-biphenyl (Li-Bp), Li 9,9-dimethylfluorene (Li-DiMF), and Li-naphthalenide (Li-NaPh) with low redox potential (≈0.33, 0.22, and 0.35 V vs Li^+/Li, respectively) can react with various anodes (such as Al, P, Sn, SnO_2, etc.) with higher lithiation potential. Through direct lithiation reaction between Li-Bp solution and SnO_2/C nanocomposite at the electrode level, the corresponding initial Coulombic efficiency was increased from 45% to 90% after 5 min treatment.[42] Similar methods were also conducted for the red P, Sn, and P/C anodes, and increase in initial Coulombic efficiency was realized.[43,44] Also, by applying Li-DiMF solution to Al foil anode, Li–Al alloy layer with thickness of ≈20 µm was formed on the surface of the electrode, which provided adequate active lithium-ion capacity to pair with Li-free S@N-C cathodes and achieved stable cycling of 100 cycles.[45] Although significant progress has been achieved for the Li-arene solutions, the prelithiation of Si-based anodes is still lacking, which possesses low lithiation potential of ≈0.25 V (vs Li/Li^+). For example, Li-NaPh prelithiation reagents with redox potential of ≈0.35 V could help to preform SEI on Si (with formation potential above 0.5 V) but could not form lithium silicide.[40] The prelithiation of Si-based anodes could be realized by employing Li-Bp derivatives with lower redox potential (<0.2 V vs Li/Li$^+$). By simply immersing SiO_x electrode into Li-Bp derivative solution, active Li was successfully introduced into SiO_x and a high initial Coulombic efficiency of ≈100% was obtained.[46]

Direct solid phase reaction between metallic Li and active materials provide an alternative way to introduce active Li into anodes. Mechanical ball milling of metallic Li powders (or Li chip) and Si powders[47,48] was explored to fabricate Li–Si alloy, which was challenging for chemical solution prelithiation using organolithium compounds, and thus adequate active lithium was introduced into the Si anodes. Li–Si alloy was successfully fabricated via the reaction between molten metallic Li and Si powder. The initial Coulombic efficiency increased from 52.6% for the pristine Si to 93.8% for the lithiated product.[49] This approach utilizing the chemical reaction between molten Li and anode materials was effective and time-saving, and could be easily extended to other alloy-type materials (e.g., Sn, Ge, Al, etc.).

Recently, one-step mechanical prelithiation strategy was conducted to solve the issue of inherent ultralow initial Columbic efficiency for the free-standing Sn based foil anodes. Through roll-to-roll calendering operation of stacked Li and Sn foils, the spontaneous reaction on their interphase between metallic Li and Sn foil produced Li_xSn layer on the surface of Sn foil and formed a Li_xSn/Sn electrode where the unlithiated Sn foil substrate served as a current collector. High active lithium-ion capacity of >3 mAh cm^{-2} was introduced into the Sn foil electrode and a high initial Coulombic efficiency of 94% was realized for $LiFePO_4$ (LFP)||Li_xSn full cells.[41] The effect of the grain refinement by using Sn-based foil for the initial Coulombic efficiency, uniformity of the lithiation, and the cycling stability was further studied in some other publications.[50] Such strategy could be extended to other Al-based foils to improve their initial Coulombic efficiency,[51] providing an extensive strategy for prelithiation of other alloy-type metal foil anodes.

Electrochemical prelithiation is a universal approach to introduce active Li for various anode materials. By discharging an assembled Li metal half-cell, accurate amount of active Li can be introduced into the anode with controlled cut-off voltage. A more facile route of direct contact between metallic Li and Si nanowires (SiNWs) with electrolyte intermediate can lithiate the SiNWs by the self-discharging effect with applied external pressure to replace the above complicated and time-consuming electrochemical prelithiation route.[28] By controlling the contact time, a high prestored lithium-ion capacity of ≈2000 mAh g^{-1} was achieved, indicating good feasibility of this direct contact electrochemical prelithiation method. In comparison to mechanical roll-to-roll operation, much lower applied pressure was required for such electrolyte-mediated electrochemical prelithiation (e.g., ≈30 MPa for mechanical roll-to-roll operation vs ≈60 kPa for electrolyte-mediated electrochemical prelithiation), and thus can be applied to electrodes with low mechanical stability. For example, Li–Al alloy layer was formed on the Al foil through such an electrolyte-mediated electrochemical prelithiation method and the initial Coulombic efficiency of full cell with LFP cathode increased to 101.4% in comparison to 86.4% for the counterpart without anode prelithiation.[28] To adjust the rate and uniformity of this electrochemical prelithiation method, a resistance buffer layer (RBL, poly(vinyl butyral) coated carbon nanotube film) was designed and inserted between Li foil and SiO_x electrode. The soft feature and high electrical conductivity of the RBL layer endowed fast and uniform prelithiation of SiO_x anode.[52]

High-capacity Li-containing species were also extensively studied as anode prelithiation additives to compensate the huge initial Li loss. SLMPs were explored and used as anode additives, which possess lowest working potential, and highest specific capacity. The superior electrochemical features of SLMPs make them suitable for the prelithiation of Si-based anodes with low initial Coulombic efficiency, which was extensively studied for Si-carbon nanotube[53] and Si nanoparticles[54] anodes. Very recently, the effect of using different amounts of SLMPs on the initial Coulombic efficiency of SiO anode was investigated in detail.[55] With different amounts of SLMPs, the initial Coulombic efficiency of SiO electrodes could be easily adjusted from 60% to 120%, which make Si-based anode feasible in practical high-energy-density batteries. Besides the SLMPs, Li_xSi alloy nanoparticles were also synthesized and successfully introduced into Si electrodes.[26] Using Li_xSi as the prelithiation additive to Si-based anode, it not only can donate high lithium-ion capacity but also can work as active materials. After introducing Li_xSi additive into Si anodes, active Li in the Li_xSi could participate in the entire electrochemical reaction and be redistributed in the entire electrode during the following cycles. Various cell systems and prelithiation strategies were discussed above, which introduced considerable lithium-ion capacity and increased initial Coulombic efficiency for the related anode materials/electrodes. To clearly show the donable capacity/prelithiation efficiency for different prelithiation strategies, the comparison of initial Coulombic efficiency for the electrodes before and after prelithiation is summarized in **Table 1**.

Besides introducing extra active Li at the anode side, lithium compensation at cathode can be an alternative strategy. To realize lithium compensation at the cathode side, two strategies were widely adopted, including using cathode prelithiation additives and direct (over)lithiation of cathode by chemical or electrochemical methods. As cathode prelithiation additives, specific designed prelithiation reagents/materials with high donable lithium ions are desirable. The donable lithium-ion capacity refers to the difference of the charge capacity and discharge capacity of the cathode prelithiation reagents/materials during the cut-off working potential range of cathode. The cathode prelithiation additives should display much higher specific lithium-ion capacities than the active materials. At the early stage, ternary $Li_xM_yO_z$ (M = Ni, Co, Fe, etc.) materials were investigated as cathode prelithiation additives, such as Li_6CoO_4,[24] Li_2NiO_2,[57,58] Li_2CuO_2,[58] and Li_2MoO_3.[59] However, these compounds often delivered low donable lithium-ion capacities (e.g., <400 mAh g^{-1}). For example, Li_2NiO_2 released a capacity of 340 mAh g^{-1} during charge process and took in a capacity of 83 mAh g^{-1} during discharge process in the cut-off potential range from 3.5 to 4.4 V (vs Li/Li$^+$), showing an overall low donable lithium-ion capacity of 257 mAh g^{-1}.[56] Some other lithium-containing salts were also explored for cathode prelithiation with insufficient theoretical donable lithium-ion specific capacities (usually from 300 to 570 mAh g^{-1}), including $Li_2C_4O_4$, $Li_2C_2O_4$, $Li_2C_3O_5$, and $Li_2C_4O_6$.[25] Li_5FeO_4 delivered a higher donable lithium-ion specific capacity (≈700 mAh g^{-1}) in the

Table 1. The comparison of initial Coulombic efficiency (ICE) for the electrodes before and after prelithiation.

Anodes	Cell configuration	ICE before prelithiation	Prelithiation strategy	ICE after prelithiation
SnO_2/C[42]	Li‖SnO_2/C	45%	Li-Bp	90%
P/C[44]	Li‖P/C	74%	Li-Bp	93%
Si[40]	Li‖Si	74%	Li-Np	96.1%
SiO_x[46]	SiO_x ‖NMC532	37.8%	Li–arene	86.4%
Si[47]	Li‖Si	54%	Ball milling	95.2%
SiO_x[49]	Li‖SiO_x	52.6%	Molten Li	93.8%
Sn foil[41]	Sn‖LFP	21%	Roll-to-roll	94%
Al foil[86]	Al‖LFP	86.4%	Electrochemical	101.4%
SiO_x[52]	NCM622‖SiO_x	75.4%	Electrochemical	89.2%
Si[54]	Li‖Si	65%	SLMPs	>100%
SiO[72]	Li‖SiO	68.1%	SLMPs	98.5%
Si[26]	Li‖Si	76%	Li_xSi	94%

cut-off potential range from 3.5 to 5 V during the first charge process.[60] However, the gas release during the charge process limited its further application.[61,62]

Binary lithium compounds can provide much higher theoretical capacities than ternary lithium containing salts. Typically, Li_3N exhibited the highest theoretical gravimetric capacity (2308.5 mAh g^{-1}) among all the investigated cathode prelithiation additives. In our previous research, stabilized Li_3N powder with crystalline Li_2O and Li_2CO_3-surface passivation layer displayed a high donable lithium-ion specific capacity of 1761 mAh g^{-1}.[27] The uniform composite of Li_2O and $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (2:5 in weight) provided a high specific charge capacity of 1083 mAh g^{-1} with cut-off charge voltage of 4.7 V (vs Li^+/Li), with additional lithium contribution from the decomposition of Li_2O.[62] Similarly, Li_2O_2 and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (5:1 in weight) composite electrode exhibited an overall charge specific capacity of 1154 mAh g^{-1}, in which $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ worked as both the active material and catalyst for the decomposition of Li_2O_2.[64] One common issue of these binary lithium compounds is that their decomposition process produces undesirable gases, which are harmful for practical battery application.

The construction of metal/binary lithium compound composites can change the decomposition reaction mechanism of simple binary lithium compound and avoid the generation of free gases, utilizing (inverse) conversion reaction mechanism, and also maintaining the advantage of high donable lithium-ion specific capacities. M/Li_2O, M/LiF and M/Li_2S (M = Fe, Co, Ni, Mn, etc.) nanocomposites were synthesized through chemical conversion reaction with molten Li using M_xO_y, M_xF_y, and M_xS_y as the raw materials. As a typical example, a Co/Li_2O nanocomposite featuring Co nanoparticles embedded in Li_2O matrix exhibited a high donable specific capacity of 619 mAh g^{-1} in the initial cycle in the cut-off potential range between 2.5 and 4.1 V.[8] Similarly, Co/LiF and Co/Li_2S nanocomposites showed high donable lithium-ion specific capacity of 516 and 683 mAh g^{-1}, respectively.[37,65] Very recently, a M/Li_2O/LiF nanocomposite with metal in a hybrid Li_2O and LiF matrix delivered a high donable lithium ion capacity of 550 mAh g^{-1}.[39] While the employment of cathode prelithiation additives has to be introduced during slurry mixing and fabrication, introducing extra active Li into each particle of active materials provides an alternative approach. Overlithiation of cathode materials represents a new research direction, which not only brings in extra active lithium for lithium compensation, but also avoids the potential harsh battery fabrication condition that regular battery prelithiation requires. To fully explore inverse conversion reaction for cathode lithium compensation, our group further combined conversion materials into commercial $LiCoO_2$ cathode. Utilizing the continuous conversion reaction between $LiCoO_2$ and lithium to form Li_2O/Co, we reported the fabrication of $LiCoO_2$ with a conformal Li_2O/Co nanoshell with thickness of ≈20 nm synthesized by in situ chemical reaction using Li-Naph solution as the reaction reagent, and an increase in overall charge capacity of 15 mAh g^{-1} was achieved for $LiCoO_2$ with 1.5 wt% Li_2O/Co. As a demonstration, full cell with such $LiCoO_2$ cathode and graphite-SiO anode delivered a high discharge capacity of 2.6 mAh cm^{-2} at 0.1C in contrast to 2.34 mAh cm^{-2} for the counterpart using pristine $LiCoO_2$ cathode.[66] Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ cathode with surface Li concentration gradient was further explored in our studies using in situ chemical prelithiation approach; a 3 Ah-class pouch cell consisting of such overlithiation cathode and Si/graphite anode displayed a high energy density of 427 Wh kg^{-1} with 11% increase in comparison to the counterpart with pristine $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ cathode.[38]

Multivalence of transition metals and abundant vacancies in the crystalline structure of cathode materials provide opportunities to directly involve active lithium into the structure of cathode and works as extra lithium for lithium compensation. By chemical treatment of $LiMn_2O_4$ cathode with *n*-butyl lithium, extra active lithium can be inserted into octahedral sites of spinel $LiMn_2O_4$, forming $Li_{1+x}Mn_2O_4$.[67] In addition, $Li_{1+x}Mn_2O_4$ can also be synthesized by heat treatment of mixed $LiMn_2O_4$ and LiI powder in an evacuated sealed ampule at 150 °C.[68] Furthermore, excess lithium was introduced into 16d site of the spinel structured $LiMn_2O_4$ to form $Li_{1.75}Mn_2O_4$, via an electrochemical approach at electrode level, which could be extracted during the potential range of 2.2–4.3 V. As a result, the overall charge capacity increased from ≈120 mAh g^{-1} for the pristine $LiMn_2O_4$

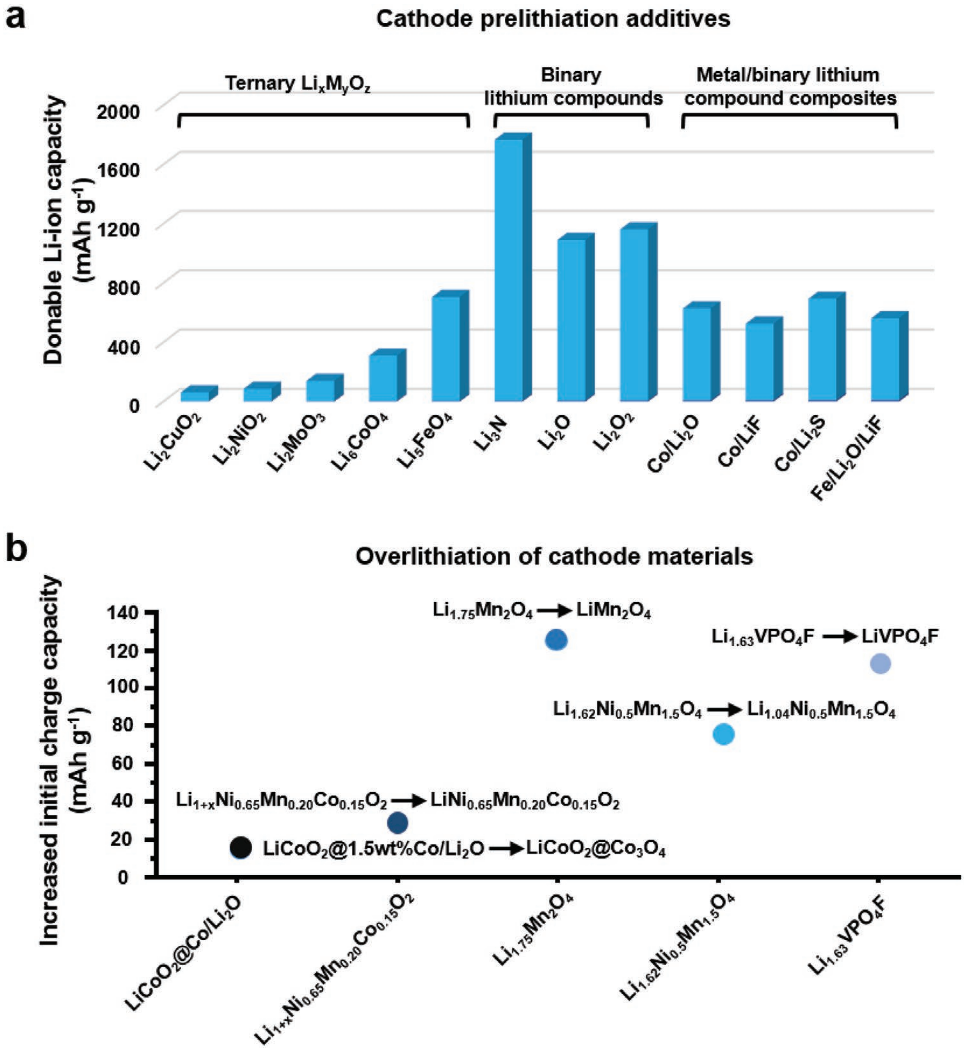

Figure 2. a) Donable lithium-ion capacities for various cathode prelithiation additives and b) excess initial charge capacities introduced by overlithiation of specific cathodes. The overlithiation degrees for specific cathodes were marked, accordingly. All gravimetric capacities were extracted from the related literatures.[8,24,27,37–39,56,58–60,63–66,69,71,98]

to ≈245 mAh g^{-1} for the as-formed $Li_{1.75}Mn_2O_4$ at 100 mA g^{-1} with the same cut-off charge potential.[69] Similarly, additional active lithium can be inserted into octahedral sites of Ni-doped spinel $LiNi_{0.5}Mn_{1.5}O_4$ to form $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ using LiI in aceronitrile as the reaction reagent at 80 °C.[70] Moreover, extra lithium was introduced into Tavorite phase $LiVPO_4F$ to form $Li_{1.63}VPO_4F$ by an electrochemical prelithiation strategy at electrode level, utilizing the $V^{3+/2+}$ redox couple. Note that such extra lithium could be extracted during the charge process of cathode below 3.5 V vs Li^+/Li, which increased overall charge capacity from ≈100 to ≈210 mAh g^{-1}.[71] The donable lithium-ion capacity and excess lithium-ion capacity for prelithiation additives and overlithiation materials respectively, are shown in **Figure 2**.

4. Chemical and Ambient Stability of the Prelithiation Materials/Reagents

The ambient stability of prelithiation materials involves the ability to resist the corrosion of ambient conditions such as oxygen and moisture. The chemical stability mainly involves the chemical reactivity of prelithiation materials with the solvents (e.g., NMP and water) used for the slurry mixing and casting processes. The higher the chemical and ambient stability of the prelithiation reagents/materials, the lower the environmental requirements for storage, which in turn translates to fewer restrictions on the preparation conditions of electrodes and better compatibility with the existing battery production process.

Despite the high specific capacities of anode prelithiation additives such as metallic Li and Li-Metal (Li-M) alloy particles, their high reactivity remains a significant concern for practical application, which relates to the safety and feasibility to the electrode preparation processes. In comparison with pure metallic Li, SLMPs with the protection of a passivation layer exhibit better stability and have been intensively studied as prelithiation additives for various electrodes.[54,72] SLMPs can be introduced into electrodes by mechanical calendering or solution dropping/casting routes. For example, prelithiation of Si-carbon nanotubes electrodes was successfully realized by directly dropping 3% SLMPs/toluene solution onto the electrode followed by thermal evaporation to remove the residual toluene (**Figure 3**a).[52] However, such operation process is not compatible with slurry fabrication process in current battery industry, since SLMPs possess high reactivity with solvents such as water and NMP for slurry, and the powder state of SLMPs poses serious safety concern during their application.

Besides powders of metallic Li, other forms of metallic Li, such as thin Li foil/layer with reduced specific surface area can be alternative choices. After passivation with organic polymer, the chemical and air stability of electrochemically deposited metallic Li layer can be further improved. As shown in Figure 3b, poly(methyl methacrylate) (PMMA) was chosen as the protection polymer for electrochemical deposition of metallic Li layer. Due to the protection of the PMMA layer, good air stability was obtained for the metallic Li layer for the prelithiation of electrode consisting of Si nanoparticles. After 30 min exposure in air with 10% humidity, Si/PMMA/Li electrode delivered a high capacity retention of 58% after 100 cycles, approaching that without air exposure (63% capacity retention), as shown in Figure 3c.[72] A Li foil was sealed between two Si-graphite loaded carbon fiber film electrode, followed by sealing the edge with conductive adhesive. Lithiation reactions occurred at the Li/Si-graphite interface assisted by mechanical rolling, and good moisture resistance was realized due to the good sealing effect of the surface hydrophobic Si-graphite electrode and conductive adhesive.[73]

Li–M alloy prelithiation additives also face high reactivity to ambient air and solvents for slurry, and need to be stabilized before their application. Taking Li_xSi powder as an example, the inherent high reactivity makes it corrosive in ambient air

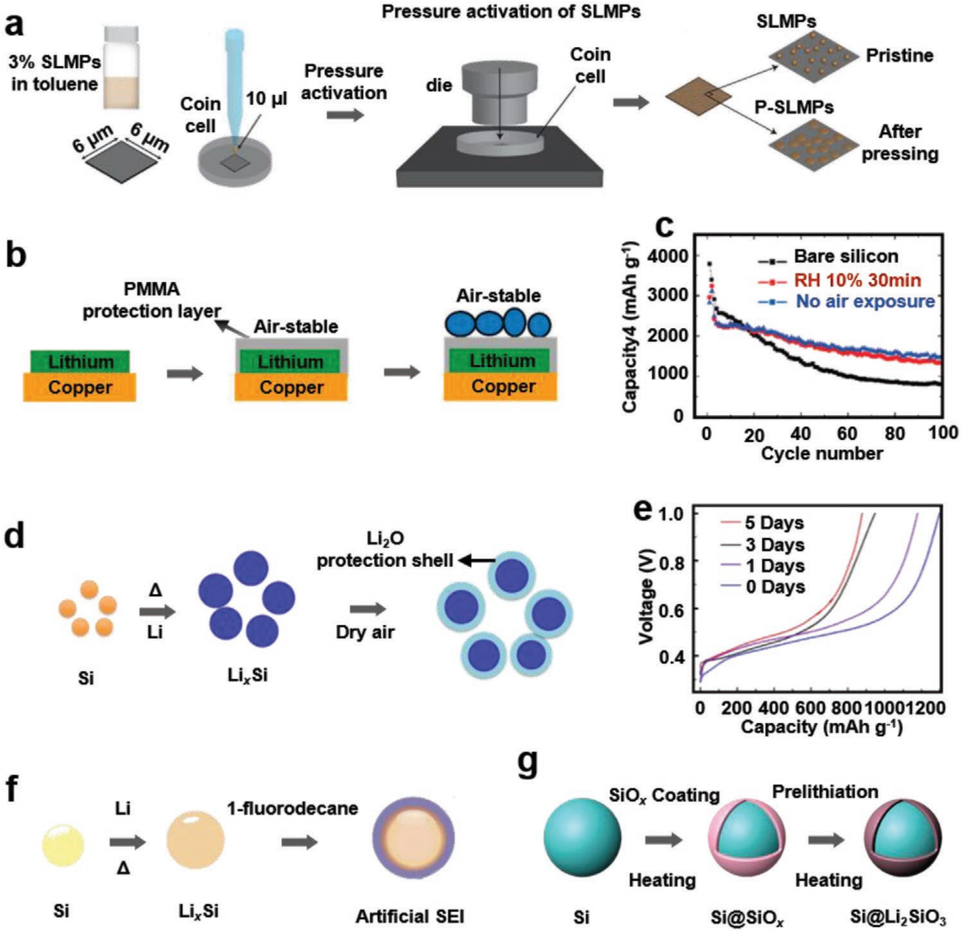

Figure 3. a) Intergration of SLMPs into electrode by dropping and pressing approach. Prelithiation reaction between SLMPs and electrode take places after pressing operation with the exposure of active Li to electrolyte. Reproduced with permission.[28] Copyright 2020, American Chemical Society. b) Prelithiation utilizing a PMMA-protected Li metal deposition layer and (c) the cycling stability of pristine Si electrode and Si/PMMA/Li electrodes (before and after exposed to air with 10% relative humidity for 30 min). Reproduced with permission.[73] Copyright 2016, American Chemical Society. d) Fabrication of Li_xSi-Li_2O core-shell structure through the reaction between Si particles and molten metallic Li,and subsequent exposure to dry air and (e) its capacity retention after exposure in dry air for different times. Reproduced with permission.[54] Copyright 2014, Macmillan Publishers Limited. f) Construction of hydrophobic LiF and Li alkyl carbonate protection layer utilizing the reaction between Li_xSi and 1-fluorodecane, leading to good air stability with moisture. Reproduced with permission.[75] Copyright 2015, American Chemical Society. g) Fabrication of Si@Li_2SiO_3 core shell structure through a SiO_x coating and thermal reaction with Li_2SiO_3. Reproduced with permission.[77] Copyright 2019, American Chemical Society.

and solvents for slurry, leading to large capacity loss. Due to the protection of Li_2O shell, an elaborately designed Li_xSi/Li_2O core–shell structure showed good dry air stability and exhibited high capacity retention of 70% after resting in dry air for 5 days. (Figure 3d,e).[26] To further improve the environmental stability, especially in the ambient condition with moisture, an artificial SEI strategy was developed for the protection of Li_xSi.[75] After reaction with 1-fluorodecane, hydrophobic LiF and Li alkyl carbonate were in situ formed on the surface of Li_xSi, and worked as protection species for moisture. The as-fabricated Li_xSi showed high capacity retention of ≈60% after exposure at ambient condition with 40% relative humidity for 6 h (Figure 3f). Despite the significant progress in improving the ambient air stability of prelithiation additives, the chemical stability to higher polar organic solvents for slurry (e.g., NMP) is far from sufficient, not to mention water.

Although considerable progresses have been achieved for the stabilization of the high-capacity Li-containing prelithiation materials, they are still insufficient for application in the practical slurry mixing and casting in battery industry. To avoid the high reactivity of the above-mentioned prelithiation materials, the exploration of inactive Li-containing materials (e.g., lithium-containing binder, lithium-containing shell structure on active material, etc.) that reduces the lithium loss during battery cycling is attractive. For example, the replacement of polyacrylic acid (PAA) binder, a classical binder for Si-based electrode, with Li-PAA, the initial lithium loss of electrodes can be reduced and the initial Coulombic efficiency can be improved.[76] With relatively lower capacity than pristine Si, SiO_x exhibits much more stable cycling than pristine Si, but encounters large lithium loss during the initial charging process. By utilizing the reaction between Li_2CO_3 reaction reagent before cycling, $Si@SiO_x$ transformed into $Si@Li_2SiO_3$ and exhibited good slurry compatibility and high initial Coulombic efficiency. The as-designed $Si@Li_2SiO_3$ composite showed a high initial Coulombic efficiency of 89.1% in sharp contrast to 56.8% for the pristine Si.[77] A $Si/SiO/Li_2SiO_3@C$ composite also delivered increased initial Coulombic efficiency of 69.05% in sharp contrast to 12.29% for pristine SiO electrode (Figure 3g).[78]

Ternary $Li_xM_yO_z$ (M = Ni, Co, Fe, etc.) additives such as Li_5FeO_4 and Li_2NiO_2 often have inferior ambient stability, and the alkaline nature of side products leads to poor slurry stability during electrode fabrication.[61,79,80] With much higher specific capacity, Li_3N powder reacts with moisture quickly and displays fast materials degradation in ambient air condition, and it is also incompatible with solvents (i.e., tetrahydrofuran (THF), NMP, and water) for the slurry processing.[81] A surface passivation layer of crystalline Li_2O and Li_2CO_3 helped to improve the ambient stability of Li_3N. Moreover, low-polarity solvent of THF was used for the slurry processing, suggesting the potential compatibility of slurry approach.[27] The integration of strong alkaline compounds with high lithium content into the electrode as prelithiation additives/active materials can lead to reaction with organic polar solvents (e.g., NMP) for battery slurry. The hydrogen (α-H) in NMP is liable to reaction with lithium-containing compounds due to the alkaline catalytic reaction mechanism, leading to severe chemical reaction between these compounds and NMP (**Figure 4**a)[82] Despite relatively higher decomposition potential, Li_2O and Li_2O_2 possess better stability in comparison to Li_3N, and are potentially compatible with slurry processing using regular PVDF binder and NMP solvent in dry air condition once the toxicity of their alkaline products is suppressed.[63,64,83] With introduction of metal to lithium compounds, metal/lithium compounds nanocomposite based on "inverse conversion reaction" showed improved ambient and chemical stability.[8,37,65] Impressively, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ with 4.8 wt% metal/LiF/Li_2O nanocomposites were successfully fabricated in ambient condition, and delivered increased charge capacity of 31 mAh g^{-1} at an industrial cathode mass loading of 20 mg cm^{-2} (Figure 4b). Due to its good resistance to H_2O and CO_2, and uniform distribution in the metal/LiF/Li_2O nanocomposites, LiF significantly improves its moisture stability, making it compatible with the existing positive electrode fabrication processing. 65% of the initial lithium-ion capacity was maintained after its storage in ambient condition for 48 h (Figure 4c).[39]

Overlithiation of cathodes can provide extra lithium for lithium compensation. Overlithiation creates built-in prelithiation reagent in each active material and is an alternative choice of using prelithiation additives. With the regular slurry and electrode processing in ambient air, we showed that a conformal Li_2O/Co prelithiation nanoshell (1.5 wt%) on commercial $LiCoO_2$ delivered an excess lithium-ion capacity of 15 mAh g^{-1} in comparison to the pristine $LiCoO_2$ (Figure 4d). Even after 12 h of exposure to ambient air, the overlithiated electrode still showed higher lithium-ion capacity of 7 mAh g^{-1} than the pristine $LiCoO_2$, showing much better stability than many other prelithiation materials (Figure 4e).[65] As shown in Figure 4f, the strategy of direct chemical overlithiation was applied to $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ cathodes. The electrode fabrication for as-fabricated overlithiated Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ can be conducted in ambient condition using regular NMP solvent and PVDF binder. Note that pristine $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ shows moisture sensitivity and is often processed in dry room in industry. In principle, this issue can be addressed by surface protection strategies, since that the reaction between Li-rich surface of materials and H_2O in ambient condition or solvents would be suppressed due to their physical isolation. Also, slurry processing in dry air condition and using water-free solvents can help to avoid this issue. Such overlithiation does not bring more harsh conditions for battery fabrication and thus is promising for practical implantation in industry.[38] Interestingly, even after exposure in ambient air for 3 h (30% humidity), the Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ still delivered an initial charge capacity of 204 mAh g^{-1}, which is 8 mAh g^{-1} increase in comparison to pristine $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ without exposure (Figure 4g).

Chemical prelithiation of electrodes involves the utilization of Li-arene solutions as the reactive reagents, which work for both anode and cathode. It is noted that the good stability of these Li-arene solutions can be realized by adjusting the concentration of the corresponding solutions. For example, a 10×10^{-3} M Li-Bp/THF solution would deteriorate quickly after being exposed to ambient air. When the concentration of Li-Bp/THF solution was increased to 1 M, the solution endured over two weeks due to the formation of surface passivation layer (Figure 4h).[43] Besides the application of these prelithiation reagents to active materials, chemical

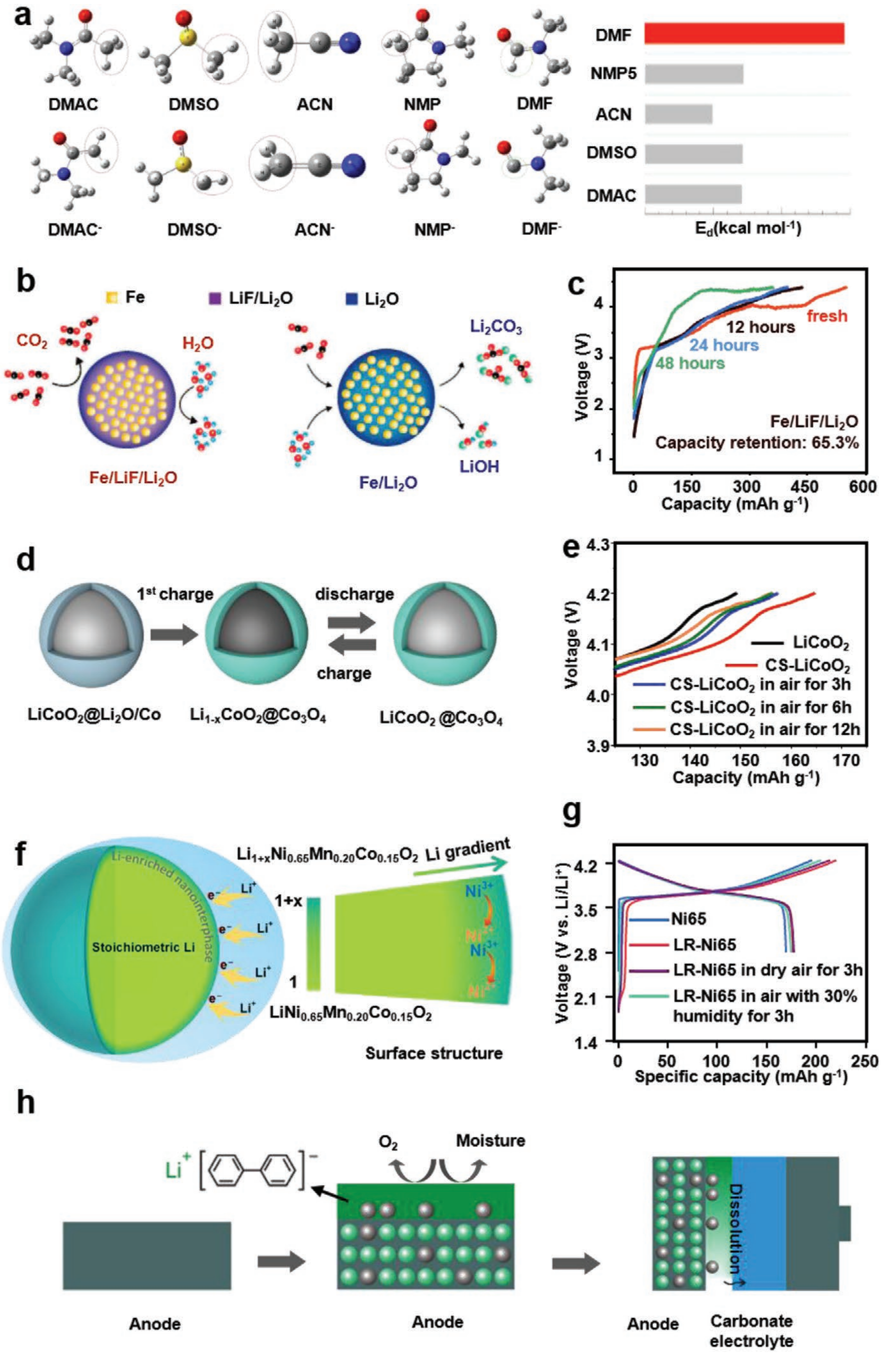

Figure 4. Chemical and ambient stability of cathode prelithiation. a) DFT calculations for possible reactions between Li_3N with different organic solvents (e.g., DMAC, DMAC-, NMP, NMP-, DMSO, DMSO-, DMF and DMF-) and their dehydrogenation energy, among which DMF shows largest dehydrogenation energy. High dehydrogenation energy can lead to good stability of Li_3N in the corresponding solvent. Reproduced with permission.[82] Copyright 2019, Science China Press. b) Schematic of chemical and ambient stability of Fe/LiF/Li_2O and Fe/Li_2O nanocomposites, and c) capacity retention of Fe/LiF/Li_2O nanocomposite after different resting times in ambient air with 20% humidity. Due to the protection of hydrophobic LiF, Fe/LiF/Li_2O nanocomposite shows improved stability. Reproduced with permission.[39] Copyright 2019, American Chemical Society. d) Schematic illustration of overlithiated $LiCoO_2$ during charge/discharge processes. The initial Co/Li_2O nanolayer converts to Co_3O_4 during the initial charge process, which remains stable during the following cycling. e) The initial charge capacities of overlithiated $LiCoO_2$ with 1.5% Li_2O/Co after exposure in ambient air condition with different times. Reproduced with permission.[66] Copyright 2020, American Chemical Society. f) Structure illustruction of overlithiated Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$, with Li-enriched gradient and regulated Li/Ni at the surface, and g) Initial charge capacities of such overlithiated Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ after exposed to various environmetal conditions and times. As comparison, initial charge capacities of pristine Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ were also measured. Reproduced with permission.[38] Copyright 2020, American Chemical Society. h) Stabilized prelithiated negative electrode with concentrated Li-Bp solutions. Using 1 м Li-Bp as prelithiation reagent, a moisture and oxygen resistant protection layer forms on the surface of the prelithiated electrodes. Reproduced with permission.[43] Copyright 2019, American Chemical Society.

prelithiation at the electrode level does not involve the slurry processing of using prelithiation additives, and thus a prefabricated electrodes before prelithiation can avoid the issue of high chemical reactivity of prelithiation additives to solvents for slurry, which is potentially more practical for industry application.

The stability of prelithiation additives plays an important role in practical applications. Surface passivation and nanocomposites of prelithiation materials could improve the ambient stability for storage and chemical stability for solvents in slurry processing. They often face challenges when they are integrated into electrodes or batteries during regular slurry processing and electrode baking. Prelithiation at electrode level can avoid the stability issues that prelithiation of active materials powder faces during the consequent slurry mixing, casting and electrode baking processes, making it feasible for potential application. To realize uniform and effective prelithiation at the electrode level, it is highly desirable to explore chemical prelithiation reagents with high safety and good stability. In addition, it is worth noting that solvent-free electrode manufacturing approaches can effectively avoid the chemical reactions between lithium-rich compounds and polar solvents (e.g., NMP and water), which is promising for the practical application of prelithiation in battery industry.

5. Safety Hazards of Prelithiation

The processing of battery prelithiation involves the fabrication of highly reactive prelithiation materials, their storage, and integration into electrodes, during which safety issues can take place. The fabrication of prelithiation materials often involves raw materials with high reactivity (e.g., metallic Li), harsh conditions (e.g., high temperature, high pressure), and high chemical heat release. For example, to synthesize Li–M alloys as anode prelithiation additives and metal/lithium compounds for cathode prelithiation additives, highly reactive metallic Li and metal particles are used as raw materials, and high processing temperature (e.g., > 180.5 °C, melting point of metallic Li) is widely adopted, which further increases the potential safety hazard during fabrication. Typically, Li_xSi alloy for anode prelithiation could be synthesized by the reaction between molten Li and Si nanoparticles at 200 °C for 6 h under continuous stirring, causing severe safety hazards during operation (**Figure 5**a). As shown in Figure 5b, for cathode prelithiation, Li_2O/Co, Li_2S/Co and LiF/Co nanocomposite additives were successfully prepared via chemical conversion reaction between molten metal lithium with Co_3O_4, CoS_2, and CoF_3 with mechanical stirring.[8,37,65] Alternatively, high energy ball milling of metallic Li and metal powders can be conducted at room temperature to produce Li–M alloys, however, it would cause more severe safety issues due to the ultrahigh reactivity of active powders, especially for nanomaterials with high surface area. The integration of prelithiation materials into electrodes may also cause safety issues due to their high activity. Many prelithiation additives (e.g., SLMPs, Li–M alloys and lithium compounds) tend to react with H_2O and O_2 in ambient air and/or polar solvents (e.g., NMP), which significantly increases the potential safety hazard during the slurry and electrode fabrication process. With high lithium content, Li_3N is easily hydrolyzed in the ambient air to produce highly corrosive and irritating LiOH and NH_3 gas. Moreover, pure Li_3N particles may decompose during the electrode fabrication, causing violent burning. In this regard, stabilized Li_3N powder with a crystalline Li_2O and Li_2CO_3 passivation layer can isolate the water and oxygen in environment conditions and improve the stability.[27]

Metallic Li reacts with arene (e.g., NaPh) to produce Li-arene solutions (e.g., Li-NaPh) with high chemical reactivity, which is widely adopted for prelithiation at the electrode level. Although effective prelithiation can be realized using these Li-arene solutions, processing of such chemical prelithiation is rigorous and cannot conducted in ambient conditions. Before the realization of the final prelithiated electrode, a washing process has to be conducted to remove the residual prelithiation reagents and side products (Figure 5c).[84] Note that such process involves volatile and flammable solvents, which may also lead to severe safety issue. Moreover, inert atmosphere is required for the storage of these prelithiated electrodes due to their high reactivity. For example, Li-arene/DME (e.g., 2-methyl Bp) solution could prelithiate SiO_x electrode into Li_xSi. Before the utilization of the prelithiated electrode, organic solutions had to be employed for cleaning to remove the residual reagents. Moreover, the as-prepared Li_xSi electrode showed high reactivity and flammability, causing difficulty in storage. Overlithiation of cathode can be realized using similar process. A 0.2 M Li-NaPh/THF solution was fabricated by chemical reaction with metallic Li and NaPh/THF solution in inert atmosphere and successful overlithiation of $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ cathode was achieved using such prelithiation reagent.[38] The electrochemical prelithiation involves metallic Li foil as active Li resource, which also leads to the potential safety issues (Figure 5d,e).[85,86] Protection from the environment should also be performed for the future storage and processing of electrode after electrochemical prelithiation.

To avoid the safety issues during the use of active metallic Li in the fabrication and processing of prelithiation materials, inactive Li-containing materials were proposed for the pretreatment of electrodes to compensate lithium loss and improve the safety. For example, an electrochemical reaction strategy using an electrolytic cell was demonstrated by using inactive Li-containing materials to prelithiate the electrode, which consisted of Si as working electrode, Cu wires as counter electrode and Ag/AgCl as the reference electrode. During the processing of electrolytic cell reaction, the Li^+ in Li_2SO_4 solution diffused across the gel electrolyte and lithiated the Si electrode, where the lithiation potential could be monitored by the reference electrode (Figure 5f). Thus, a safe prelithiation process was realized in sharp contrast to the cases involving using metallic Li.[87] As mentioned above, the use of Li-PAA instead of PAA binder, and formation of Li_2SiO_3 species on Si-based anodes can increase the initial Coulombic efficiency and realize successful prelithiation with good safety.

With regard to safety, all the chemicals/raw materials, fabrication of prelithiation materials and their storage, integration into electrode, electrode baking, canlendering, and the subsequent storage of prelithiated electrode, must be taken into the consideration. Considering the high activity of active lithium-containing species, prelithiation additives and

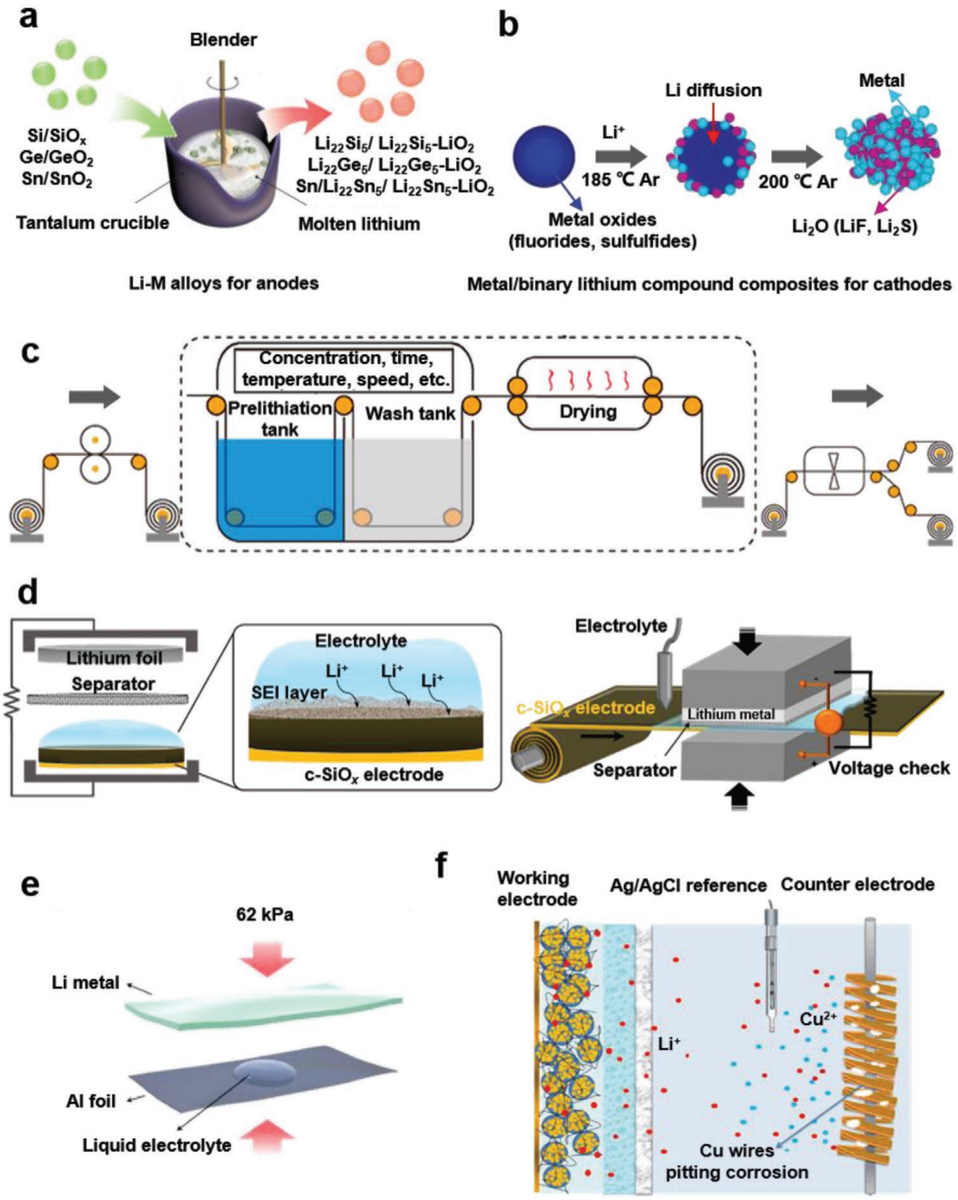

Figure 5. Safety hazards of prelithiation. a) Fabrication of Li-M alloys using alloy-type anode particles and molten Li. b) Syntheis of metal/binary lithium compound composites utilizing chemical reaction between transition metal oxides (fluorides, sulfulfides) and molten Li (e.g., $Co_3O_4 + 8Li \rightarrow 3Co + 4Li_2O$). Reproduced with permission.[8] Copyright 2016, Macmillan Publishers Limited. c) Processing of chemical prelithiation with Li-arene solution at electrode level, which involves immersion, washing and drying processes. Reproduced with permission.[84] Copyright 2020, Elsevier. d) Electrochemical prelithiation of SiO$_x$ electrode with the existence of external circuit, and e) electrochemical prelithiation of Al foil by direct with metallic Li under applied external pressure. Reproduced with permission.[85] Copyright 2015, American Chemical Society. Reproduced with permission.[86] Copyright 2020, Elsevier. f) Electrolytic cell for the prelithiation of Si electrode without the involvement of active metallic Li. Reproduced with permission.[87] Copyright 2015, Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim.

overlithiation of cathode, inactive Li-containing materials are attractive for practical battery application with high safety.

6. Residues and Side Reactions during Prelithiation

The unavoidable effects of residues and side reactions that prelithiation brings should be taken into account for their practical application in lithium-ion batteries. In this part, the residues and side reactions are discussed and the methods to avoid/reduce the negative effects of prelithiation are also provided.

The products after chemical prelithiation often involve side products besides the prelithiated materials/electrodes. For the widely used chemical prelithiation reagents such as Li-Bp, Li-NaPh, and Li-DiMF in THF/DME solutions, solid Bp, NaPh and DiMF may be left on the surface of materials/in the

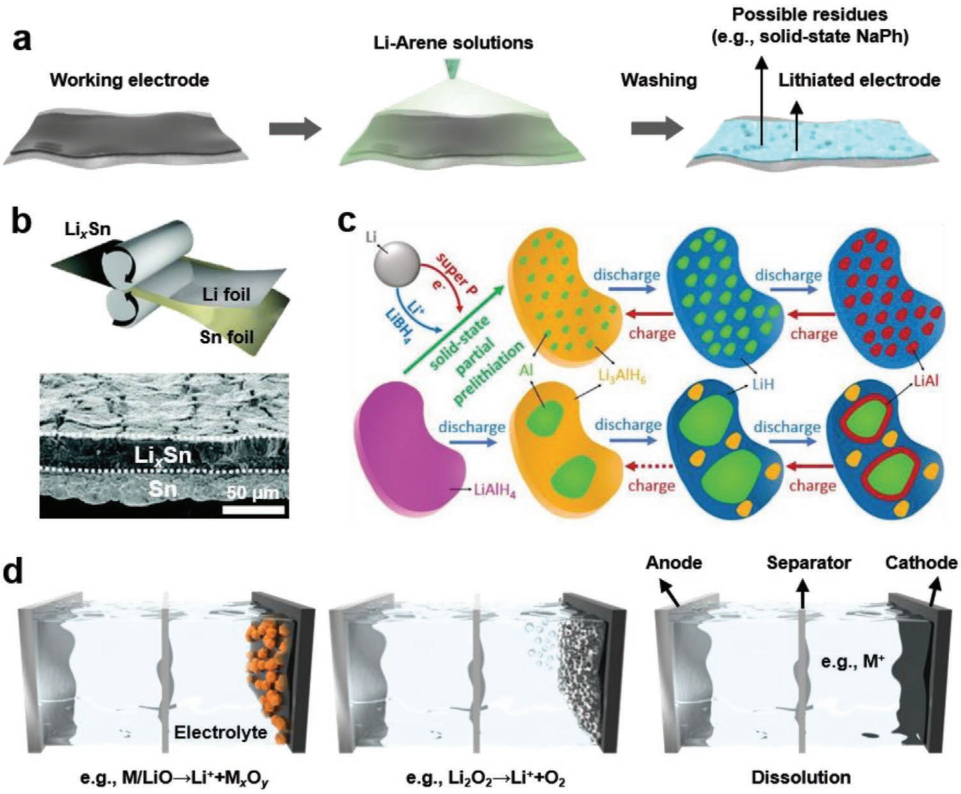

Figure 6. Residues and side reactions during prelithiation. a) Schematic of chemical prelithiation of electrode using Li-arene solutions. The solid residues can be left in the electrode, requiring additional cleaning process. b) Chemical prelithiation of Sn foil by mechinical calendering operation. Li_xSn layer was formed on Sn substrate without introduction of other residues. Reproduced with permission.[41] Copyright 2019, The Royal Society of Chemistry. c) Solid electrochemical prelithiation of a Li_3AlH_6-Al anode for solid-state batteries via heat treatment (120 °C) of hybrid consisting of $LiAlH_4$ (active material), Li (Li source), carbon black (electronically conductive additive) and $LiBH_4$ (ionic conductor). Reproduced with permission.[89] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Schematic illustrations of residues or side reactions for cathodes with prelithiation additives, including solid residuals (left), gases (middle), and dissolution of decomposition products (right).

electrodes after the evaporation of solvents, which requires repeated cleaning to avoid negative effects such as low conductivity (**Figure 6**a). Chemical lithiation utilizing the reaction between pure metallic Li and active materials can avoid the introduction of residues or inert materials. Through the reaction between active particles and molten lithium with specific designed weight ratio, products with accurate lithiation degree could be realized without any residues. The universality of this method was probed for the group IV elements (e.g., Si, Ge, Sn, etc.) and their related oxides.[88] Si, Ge, Sn, and their corresponding oxides were successfully lithiated by molten Li and a high capacity could be donated. In detail, stirring of molten Li and Ge nanoparticles at 250 °C produced $Li_{22}Ge_5$, which delivered a high charge specific capacity of 910 mAh g^{-1}. However, during the integration of these active materials into electrodes, possible side reactions can occur with chemicals such as solvents for slurry and the processing environmental conditions such as moisture. The prelithiation at electrode level through similar solvent-free reaction process can avoid the issues that processing of powder materials faces. Typically, a simple calendering operation of stacked Li foil and metal foil (e.g., Sn and Al foil) produces a Li–M alloy layer on the metal foil anode and avoids the introduction of other possible residues and side reactions, but their generalization to other forms of electrodes still face challenges (Figure 6b).[41]

Besides, the electrolyte residues in prelithiated electrodes after electrochemical prelithiation may cause negative effects for their subsequent processing and battery fabrication, especially for large-scale application in industry. Thus, it is highly desirable to explore facile approaches to remove the residual electrolytes or avoid the use of liquid organic electrolytes for the practical employment of electrochemical prelithiation.[52] Solid-phase electrochemical prelithiation method provides an alternative strategy to avoid the involvement of residual liquid electrolyte. A Li_3AlH_6-Al anode for solid-state batteries was prelithiated via heat treatment (120 °C) of hybrid consisting of $LiAlH_4$ (active material), Li (Li source), C (electronically conductive additive) and $LiBH_4$ (ionic conductor) (Figure 6c). The prelithiation degree of the product was controlled via the quantitative addition of Li and active materials.[89] As for prelithiation additives, the application of SLMPs as prelithiation additives would not cause residues in principle since they would fully take part in the lithiation of active materials. For high-capacity prelithiation additives, their volume shrinkage after lithium donation and the residual passivation structure left in the electrode may cause instability of the electrode.

Large mass residuals often remain after extracting active lithium ions from ternary $Li_xM_yO_z$ (M = Ni, Co, Fe, etc.) additives, lithium-containing salts (e.g., $Li_2C_4O_4$, $Li_2C_2O_4$, $Li_2C_3O_5$, and $Li_2C_4O_6$) and nanocomposite of metal/lithium compounds (M/Li_2O, M/LiF, M/Li_2S, and M/LiF/Li_2O, etc.) (Figure 6d left). Although some of these cathode additives (ternary $Li_xM_yO_z$) can take part in the following charge/discharge processes, their cycling stability is often inferior.[22,58,79] The generation of gases for additives of lithium-containing salts can lead to poor wettability between the electrode and electrolyte, and even destroy the structure of electrode during the working process. Meanwhile, their solid residues often possess poor electronic conductivity, deteriorating the electrochemical performance.[8,25,37,39,65] Binary lithium compounds (e.g., Li_2O, Li_2O_2, and Li_3N) with high theoretical capacities produce much larger amount of gases (e.g., O_2 and N_2) during the electrochemical extraction of active lithium, which requires additional degassing process before battery cycling application (Figure 6d middle). More seriously, these binary lithium compounds often encounter incomplete decomposition during the initial charging process, which causes continuously release of gases in the subsequent cycling. Also, the residuals due to the incomplete decomposition of these additives lower the electronic conductivity of the entire electrode.[60]

Lithium extraction from cathode prelithiation additives often takes places at higher working potential in comparison to the existing cathodes. To realize high donable lithium-ion capacities, relatively high cut-off charge potential has to be applied in the working process of these cathode prelithiation additives. The high working potential, especially beyond the stable working potential window of electrolyte (usually <4.5 V vs Li/Li^+ for commercial carbonate-based electrolytes), would aggravate the side reactions between the active cathode materials and electrolyte, which degrade the electrochemical performance. For instance, severe side reactions related to electrolyte decomposition occur during lithium extraction from prelithiation additives of Li_5FeO_4,[90] Li_2MoO_3,[91] and pure Li_2O or Li_2O_2[63,64] due to the high applied voltage (>4.7 V vs Li/Li^+). Also, the decomposition products (e.g., Mo species) of some prelithiation additives (e.g., Li_2MoO_3) would dissolve in the electrolyte, and migrate through the separator to the negative electrode, leading to side reactions at the anode (Figure 6d right).[59] Overlithiation of some specific cathode materials can introduce excess Li into their crystal structures, which can be fully extracted during the battery charging, without inert residuals or gases generation. The only remaining products are active materials that participate in the subsequent charge and discharge processes, thus maximizing prelithiation efficiency. With respect to the residues, such a prelithiation approach is ideal.[38,66,69–71] The schematic illustration of the residues or side reactions occurring for cathode during the electrochemical reactions is shown in Figure 6d.

Overall, the residuals include gases accompanied by the decomposition of prelithiation additives, inert solid species that may destroy the structure of electrode and lower the electronic conductivity. Besides, side reactions occur due to the increased cut-off charge potential for electrochemical lithium extraction, and some metal residuals can also catalytically decompose the liquid electrolyte. Currently, the studies on residuals and side reactions are still in the early stage. Deep insight into the mechanism, process, and effect on electrochemical performance is lacking. To realize the practical employment of prelithiation, more studies should be conducted on the mechanism and effects of residuals and side reactions introduced by prelithiation, and strategies for their improvement.

7. Potential Effect on Electrochemical Performance

While it is true that prelithiation can compensate lithium loss and increase the energy density of lithium-ion batteries, the involvement of prelithiation may pose potential effects on battery performance. In this part, the potential effects of prelithiation materials/methods on electrochemical performance were discussed, including reversible capacity, cycling stability, as well as the rate capability.

Taking chemical prelithiation of alloy-type foil anode (e.g., Sn and Al) as an example, the initial Coulombic efficiency of Sn foil was improved after prelithiation by using a mechanical calendering route with Li foil. For pure Sn foil electrode, the catalysis of electrolyte decomposition during the initial charging process led to intrinsic low initial Coulombic efficiency (e.g., <20%),[92] which impeded the direct use of pure Sn foil in full batteries. After prelithiation, the initial potential of the as-formed Li_xSn/Sn foil decreased to below 1 V (vs Li^+/Li), which suppressed the side reactions with electrolyte and introduced abundant active Li. When paired with LFP cathode, LFP||Li_xSn cell showed a high initial Coulombic efficiency of 94% in sharp contrast to 21% for the counterpart using pure Sn foil anode. LFP||Li_xSn cell delivered a high reversible capacity of 2.28 mAh cm^{-2} after 200 cycles, three times that the LFP||Sn cells exhibited (0.75 mAh cm^{-2}, **Figure 7**a).[41] The chemical prelithiation of metal foil electrode with increased accessible surface area to electrolyte also led to the enhanced rate capability, probably due to the increased contact area with electrolyte after prelithiation. The change in volume during the lithiation/delithiation process was another factor which prelithiation brought in. For an elaborately designed Li_xSi/graphene nanocomposite, Li_xSi at expansion state filled in the graphene gaps, and thus adequate space could be prereserved after delithiation, which could better accommodate the volume expansion during the subsequent cycling. As a result, Li_xSi/graphene||$LiFePO_4$ full cells displayed stable cycling for 200 cycles with average Coulombic efficiency of 99.92% (Figure 7b).[93]

For cathode prelithiation, the surface and bulk properties of cathode may change after chemical prelithiation or overlithiation, causing the consequent change in electrochemical performance. For example, due to the introduction of excess lithium, lithium-rich Li_2O/Co nanolayer would be produced on the surface of commercial $LiCoO_2$ during the overlithiation, which provided extra lithium during the charge process.[66] The conformal surface layer after lithium involvement may lead to different reactivity with electrolyte in comparison to the pristine $LiCoO_2$, which showed more stable cycling performance for full battery, as shown in Figure 7c. In our previous work, we show that overlithiation of $LiNi_{0.65}Mn_{0.2}Co_{0.15}O_2$ cathode not only produced a surficial Li concentration-gradient structure but also optimized the Li/Ni disorder of the bulk structure,

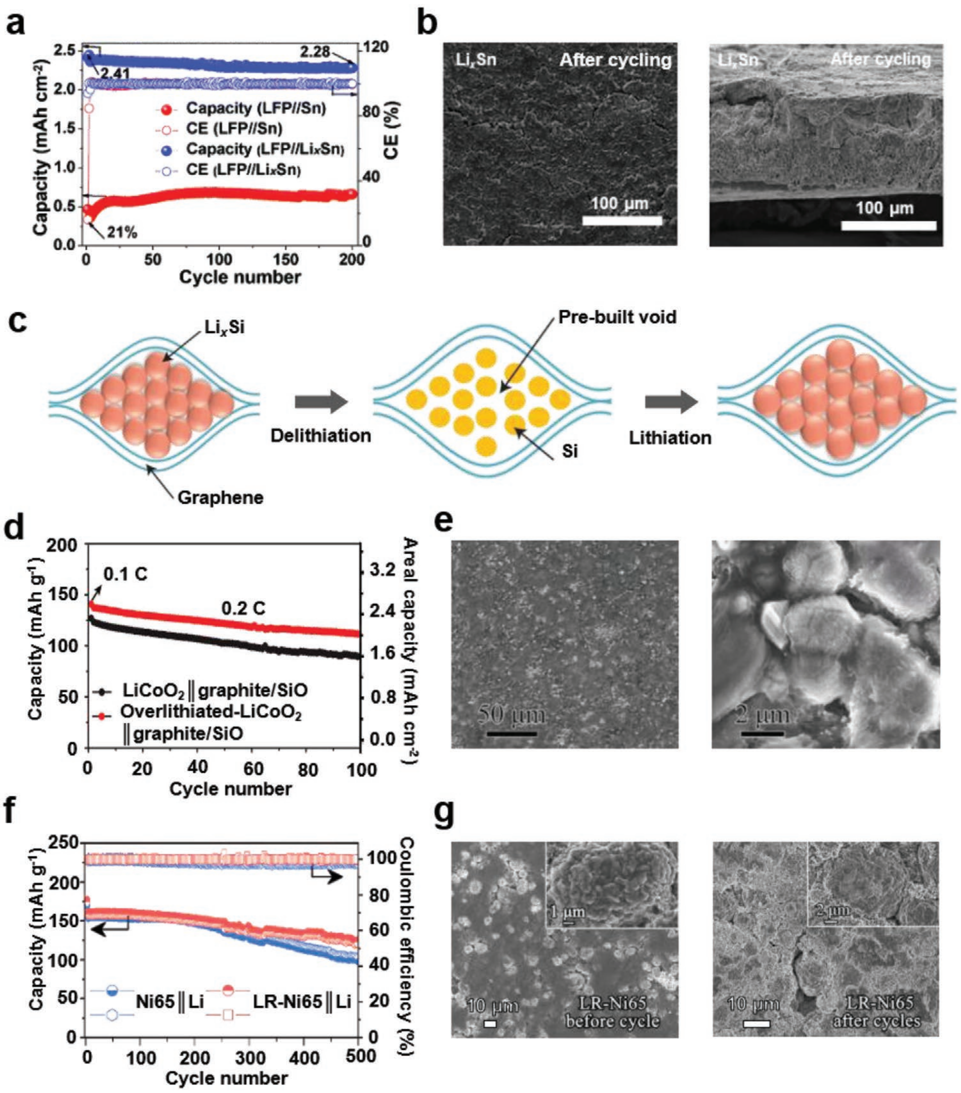

Figure 7. Potential effect on electrochemical performance for prelithiation. a) Cycling performance of Sn||LFP and Li_xSn||LFP full cells. With the increased initial Coulombic efficiency and introduction of excess active Li, the Li_xSn||LFP full cell delivered significantly higher reversible capacity and better cycling stability than the Sn||LFP full cell. b) Surface and cross-sectional SEM images of Li_xSn anode after cycling. Dense structure of the eletrode was matained, supporting the stable cycling. Reproduced with permission.[41] Copyright 2019, The Royal Society of Chemistry. c) Schematic of lithiation and delithiation of graphene-encapsulated Li_xSi nanoparticles for stable cycling. The using of preexpanded Li_xSi particles could help to accommodate the volume change during change/discharge processes. Reproduced with permission.[93] Copyright 2017, Macmillan Publishers Limited, part of Springer Nature. d) Cycling performance of the overlithiated $LiCoO_2$||graphite/SiO and pristine $LiCoO_2$||graphite/SiO full cells. With the introduction of excess lithium-ion capacity, the overlithiated $LiCoO_2$||graphite/SiO full cell displayed higher reversible capacity than the pristine $LiCoO_2$||graphite/SiO full cell. e) SEM images of the overlithiated $LiCoO_2$ electrode after 100 cycles. The initial structure of the material and electrode was maintained, suggesting that overlithiation does not cause negative effect on electrochemical cycling of $LiCoO_2$. Reproduced with permission.[66] Copyright 2020, American Chemical Society. f) Cycling performance of overlithiated $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$ (LR-Ni65) and pristine $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$ (Ni65) electrodes. The overlithiated $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$ displayed better electrochemical cycling stability than the pristine $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$, indicating the enhanced structural stability. g) SEM images of the overlithiated $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$ electrode before and after cycling. The secondary particles of the overlithiated $LiNi_{0.65}Mn_{0.20}Ni_{0.15}O_2$ remained intact after cycling. Reproduced with permission.[38] Copyright 2020, American Chemical Society.

which increased the structural stability and improved electrochemical cycling performance. As expected, the overlithiated $LiNi_{0.65}Mn_{0.2}Co_{0.15}O_2$ cathode displayed high capacity retention of 77% under 1C after 500 cycles, in contrast to 64% for the pristine $LiNi_{0.65}Mn_{0.2}Co_{0.15}O_2$ cathode under the same test condition. To show the potential application in battery industry, a 3 Ah-class pouch cell was fabricated, consisting of the prelithiated $LiNi_{0.65}Mn_{0.2}Co_{0.15}O_2$ cathode and high-capacity Si/graphite anode, and it displayed high energy density of 427 Wh kg^{-1}, 11% higher than the counterpart with pristine $LiNi_{0.65}Mn_{0.2}Co_{0.15}O_2$ cathode (Figure 7d).[38] However, overlithiation can also produce negative effect on the cycling stability of cathodes. For example, $LiCoO_2$ with 32 wt% Li_2O/Co fabricated via deep chemical overlithiation provided a much higher initial charge capacity of 470 mAh g^{-1} in comparison to the commercial $LiCoO_2$, and delivered a low reversible discharge capacity of 53 mAh g^{-1}.[66]

Cathode prelithiation additives can release high donable lithium-ion capacities to compensate the active lithium loss that the anode consumes. However, many high-capacity binary lithium compounds (e.g., Li_2O, Li_2O_2, and Li_3N) produce undesirable gases (e.g., O_2 and N_2). There undesirable gases would destroy the contact between electrolyte and active materials, cause increased impedance, and thus lead to the degradation of electrochemical cycling.[63,64] For example, despite the increase in the initial charge capacity due to the lithium contribution from Li_2O_2 additive, the hybrid electrode of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and Li_2O_2 (95:5 in weight) underwent quick capacity decay and showed a low capacity of 125.1 mA h g^{-1} after 160 cycles, even lower than the pristine $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ electrode (Figure 7e).[64] It is noteworthy that the amount of the used additives should be optimized with regard to the donable capacity of the additives and other electrochemical parameters, including cycling stability and rate capability of the electrodes. Till now, few studies have investigated the effect of cathode prelithiation additives on the rate capability of the cathode. In principle, the inert residuals and gases release would change the transport of electrons and ions, and increase the internal resistance of the electrode, which is highly related to the rate capability.

The introduction of extra lithium at cathode or anode would increase the energy density of batteries by effective lithium compensation. Meanwhile, prelithiation can bring in other effects depending on adopted prelithiation approaches. The effect of residuals, gases release and side reactions should be comprehensively considered in evaluation of the battery performance.

8. Industrial Compatibility and Scalability of the Prelithiation

Besides good electrochemical performance, industrial compatibility and scalability is the last but of key importance for the practical implantation of prelithiation materials/methods. However, few works have linked their relationship with current battery fabrication processing. In this part, we organize the discussion of industrial compatibility and scalability of prelithiation towards industry application with consideration of ambient and chemical stability, safety, and environmental hazards, as well as scalability.

SLMPs possess highest donable lithium-ion capacity, but are challenged by their integration with active materials into electrodes for industrial applications. For example, the processing of SLMPs in most literatures involves their dispersion into organic solvents such as toluene[53] and hexane[72] to form suspensions, following by dropping onto the electrode and drying. The suspensions of such SLMPs are often inhomogeneous, leading to lack of control over the amount of SLMPs that is introduced to the active electrode. Although SLMPs show good dry air stability, their light weight, high activity and flammability due to the powder nature make the scalable processing of SLMPs unsafe. Some studies reported the involvement of SLMPs into electrodes through a direct mechanical pressing without solvents, in which case the above mentioned issues would become more serious.[54] Despite the success in lab-scale operation of SLMPs, their industry application is still challenging. Li–M alloy prelithiation powder additives encountered similar issues with regard to safety during their integration into electrodes.[26] Considering the safety, prelithiation materials with low accessible surface area (e.g., thin metallic Li film[94] and metallic Li strip[95]) to the environment have more opportunities for practical industry application. Ultrathin Li films are attractive for prelithiation due to their reduced active surface and easy processing in comparison to SLMPs. However, facile fabrication approaches of ultrathin Li films with high safety remain lacking, which inhibits the practical implantation of ultrathin Li films. Recently, ultrathin Li films with thickness from 10 to 20 µm were successfully fabricated through spreading molten Li across the surface of lithiophobic substrates with organic coating and alloy elements.[96] Very recently, ultrathin Li metal/reduced graphene oxide (Li/rGO) composite films were fabricated with adjustable thickness from 0.5 to 20 µm. By simply covering such an ultrathin Li/rGO film on a Si-based anode, the initial Coulombic efficiency was increased from 79.4% to around 100%.[97] These results shows the success of using ultrathin Li films for prelithiation in high energy density batteries. However, its scalability is still challenging due to the harsh fabrication condition, complex processing, and potential high cost. Cathode prelithiation additives usually show much better environmental and chemical stability in comparison to the anode prelithiation additives and do not react with the current NMP solvent for slurry fabrication, and have good compatibility with the existing battery fabrication process. Typically, a uniform nanocomposite of $Fe/LiF/Li_2O$ showed good stability in ambient atmosphere, and exhibited high lithium-ion capacity (550 mAh g^{-1}) and high stability in ambient condition (65% capacity retention after resting in ambient condition for 48 h), benefiting from the good moisture stability of LiF, making it compatible with the existing battery fabrication process.[39]

Prelithiation at electrode level can be achieved using electrochemical prelithiation. Using Li metal half-cell configuration combined with an external circuit, one can control the lithiation degree accurately. However, the assembly and disassembly of cell and the subsequent cleaning process make such an approach difficult for scalability. Although short-circuit contact of Li foil and electrode with the electrolyte can also realize successful electrochemical prelithiation, without complex cell assembling/disassembling processes, the demands of huge external press and residuals make it challenging for scalability. Also, the nonuniformity of the lithiated product and the uncontrollability of the lithiation degree make it premature for practical application. Moreover, the introduction of Li metal foil increases safety concerns and requires complex postprocessing of used Li metal foil. Despite the success of electrochemical prelithiation at lab scale, the above mentioned issues should be addressed before its practical involvement in battery industry.

Successful prelithiation can be realized at electrode level through chemical prelithiation using Li-arene solutions. Taking the prelithiation of SiO_x electrodes as an example, the processing of such chemical solution prelithiation involves the immersion of electrode within Li-arene solutions. The lithiation degree of the electrode can be adjusted by using different reaction conditions (e.g., temperature, time, and concentration of Li-arene solution). Subsequently, the electrode should be cleaned by nonpolar solvents (e.g., THF, DME, and 1,3-dioxolane) repeatedly to remove the residual prelithiation reagents.[46] Usually, these Li-arene solutions for prelithiation are sensitive to ambient atmosphere, and thus the application of these prelithiation reagents require rigorous environmental condition in comparison to that of current battery fabrication. Meanwhile, the volatility of the solvents causes uncontrollability of the process and prelithiation degree of the final products, especially in the case of larger scale. The cathodes after chemical prelithiation using solution reaction often possess better stability in contrast to the anode counterpart, making it more promising for practical application. For example, the overlithiation cathode material Ni-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ was fabricated by a simple chemical prelithiation, and such overlithiation cathode material can be compatible with the existing battery industry for commercial $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$. Furthermore, ≈4.1% of increased charge specific capacity was still realized for such overlithiated cathode after exposure in ambient air for 3 h with 30% humidity.[38]

Prelithiation materials/methods without the involvement of additional equipment, processing, and environmental demands are highly desirable for industry application. Currently, many of reported prelithiation materials/methods have achieved success in lab scale and already showed promise in scalable application. More attention should be paid to the requirements that industry battery fabrication asks for, including the safety and environmental concerns, cost, and compatibility with industry processing.

9. Outlook

During the past years, prelithiation has become a widely adopted approach to compensate the lithium loss and improve the energy density of lithium-ion batteries, especially for high-capacity anode materials (e.g., Si based anodes). This perspective highlights the key parameters of prelithiation as well as the challenges/issues associated with prelithiation itself, including: donable lithium-ion capacity/prelithiation efficiency, chemical and ambient stability of the prelithiation materials/reagents, safety hazards of prelithiation, residues and side reactions during prelithiation (e.g., gas evolution), potential effect on electrochemical performance (e.g., inert materials/residuals introduced by prelithiation), industrial compatibility and scalability of the prelithiation. The principles and effects for various prelithiation materials/methods were discussed in detail with respect to these key parameters, and typical examples have been provided to further explain these parameters. New challenges associated with prelithiation have been analyzed, including high reactivity of prelithiation materials, safety concerns during the processing of prelithiation, and potential negative effects caused by prelithiation. We have also discussed the understanding and possible solutions to these new challenges.

Yet the scientific literature is mainly concerned with the donable capacity or increased energy density that prelithiation resulted in; other important parameters are often overlooked, especially in practical lithium-ion batteries. Further understanding the effect of prelithiation at the materials level and electrode level is needed in future works. Detailed information about the changes that prelithiation causes for active materials and electrodes is unclear due to their complexity. After the introduction of excess Li, the volume change of active materials may be affected, as well as the subsequent strain change at the materials/electrode level. Meanwhile, the Li introduction may change the surface (or even bulk) structure (e.g., SEI) and property of active materials. For example, with anode prelithiation, Si-based anodes undergo complex phase and surface structure changes at materials and electrode level, and their electrochemical performance would be changed consequently, warranting further studies in this area.

Studies of the ion and electron kinetic transport for the prelithiated materials/electrode is also important, as prelithiation may change the electronic conductivity of active materials or electrode, and further affect the rate capability. For example, some binary lithium compounds (e.g., Li_2O_2 and Li_3N) have poor electronic conductivity, leading to inferior rate capability. Also, voids can form after the decomposition of these binary lithium compounds, which destroy the mechanical stability of electrodes, as well as the electronic kinetic transport. This issue can be alleviated by using small-sized particles of these compounds and their uniform dispersion in the electrodes.

Prelithiation can offer high lithium-ion capacity and improve the energy density of lithium-ion batteries. However, it may potential cause safety concerns due to their high reactivity. The development of prelithiation materials/methods with high safety is highly desirable towards the practical application in industry. Prelithiation at electrode level can avoid the issue that direct integration of reactive prelithiation materials into electrode faces, including their reaction with polar solvents for slurry processing such as NMP. Overlithiation of cathodes at electrode level can contribute excess lithium-ion capacity and exhibit good stability. For example, overlithiation of $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ electrode would not cause harsher requirement for electrode/battery fabrication in comparison to the pristine electrode. For the practical involvement of anode prelithiation additives or prelithiation reagents with high reactivity, more attention should be placed on increasing their stability in materials and electrode processing. Although some current strategies of surface protection can realize high stability in dry air condition, such as Li_2CO_3 for SLMPs and F-based surface layer for Li_xSi particles, further improving their stability against moisture and polar solvents for slurry are of key importance for their scalable application.

It is worth pointing out that the practical employment of various prelithiation materials/methods relies on their compatibility with the existing battery industry and the cost. Direct integration of prelithiation into the state-of-art battery manufacturing is much faster than developing brand new processes or equipment. In this regard, prelithiation methods with good industry compatibility would have more chance for practical scalable application. In addition, the cost involved in prelithiation should be taken into consideration for industry application. The cost of current prelithiation materials (e.g., SLMPs) is usually high. Additional materials/electrode processing would also increase the cost of prelithiation. Therefore, it is of key importance to explore efficient prelithiation materials/methods with facile routes and low cost for future commercial applications. Initial anode-free lithium batteries employ metal collectors (such as Cu foil) as the anodes, and lithium-containing compounds on metal collectors (such as layer oxides and phosphates on Al foil) as the cathodes. Similar to Si-based (or other high-capacity lithium-free) anodes, only the cathodes provide active lithium for batteries. Metal current collectors often show low initial Coulombic efficiency and reasonable lithium loss during the initial metallic Li plating/stripping cycle. Thus, prelithiation can compensate the lithium loss at the anodes and maximize the energy density of anode-free lithium battery systems.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

donable lithium-ion capacity, industrial compatibility, prelithiation, residuals, safety hazards, stability

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