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REVIEW

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Practical evaluation of prelithiation strategies for next-generation lithium-ion batteries

Shiming Chen[1] | **Zhen Wang**[1] | **Meng Zhang**[2] | **Xiaoze Shi**[3] | **Lu Wang**[1] | **Weifeng An**[3] | **Zikun Li**[2] | **Feng Pan**[1] | **Luyi Yang**[1]

[1]School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen, China

[2]BTR New Material Group Co., Ltd., Shenzhen, China

[3]R&D Institute, Shenzhen BAK Power Battery Co., Ltd., Shenzhen, China

Correspondence
Meng Zhang and Zikun Li, BTR New Material Group Co., Ltd., 518107 Shenzhen, China.
Email: zhangmeng@btrchina.com and lizikun@btrchina.com

Feng Pan and Luyi Yang, School of Advanced Materials, Peking University Shenzhen Graduate School, 518055 Shenzhen, China.
Email: panfeng@pkusz.edu.cn and yangly@pkusz.edu.cn

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Abstract

With the increasing market demand for high-performance lithium-ion batteries with high-capacity electrode materials, reducing the irreversible capacity loss in the initial cycle and compensating for the active lithium loss during the cycling process are critical challenges. In recent years, various prelithiation strategies have been developed to overcome these issues. Since these approaches are carried out under a wide range of conditions, it is essential to evaluate their suitability for large-scale commercial applications. In this review, these strategies are categorized based on different battery assembling stages that they are implemented in, including active material synthesis, the slurry mixing process, electrode pretreatment, and battery fabrication. Furthermore, their advantages and disadvantages in commercial production are discussed from the perspective of thermodynamics and kinetics. This review aims to provide guidance for the future development of prelithiation strategies toward commercialization, which will potentially promote the practical application of next-generation high-energy-density lithium-ion batteries.

KEYWORDS
high-energy-density, irreversible capacity loss, lithium-ion batteries, practical application, prelithiation

1 | INTRODUCTION

The search for high-energy-density electrode materials has never stopped since the first commercial lithium-ion battery (LIB) was introduced in the 1990s. Compared with commercially used graphite (Gr), which shows relatively low specific capacity (372 mAh g^{-1}) and acceptable initial Coulombic efficiency (ICE, ~90%),[1–3] alternative anode materials such as hard carbons (HC), silicon (Si)-based materials, germanium (Ge), tin (Sn), and phosphorus (P)

Shiming Chen and Zhen Wang contributed equally to this study.

show significantly higher specific capacity and lower ICE.[4,5] For instance, the disordered orientation of graphene layers in HC leads to severe side reactions that lead to additional lithium loss of ~30% in the initial cycle (ICE, ~60%). With a high theoretical specific capacity of 1500–4200 mAh g^{-1}, Si-based anodes are one of the most promising candidates for next-generation batteries. Nevertheless, the relatively low ICE (60%–85%) and continuous reconstruction of the solid electrolyte interphase (SEI) film of Si-based anodes have also markedly hindered their practical application.[6] Therefore, when these anode materials are coupled with cathode materials (e.g., $LiCoO_2$ and $LiFePO_4$) with limited Li^+, the capacity of full-cells shows high irreversible active Li loss during prolonged cycling due to undesirable side reactions (e.g., electrolyte decomposition), resulting in capacity decay and structural degradation.

Hence, introduction of extra lithium sources into anodes and cathodes before cycling (i.e., prelithiation) using chemical or electrochemical methods is found to be an effective strategy to recover the energy density of full-cells.[7] Also, lithium-free cathodes (e.g., sulfur) with relatively large capacities could also be used to assemble high-energy batteries. Moreover, many methods not only compensate for the initial irreversible capacity loss (ICL) but also recover active lithium loss during the cycling process, improving battery stability in subsequent cycles. Besides, it was recently discovered that a robust SEI can be formed through prelithiation, enabling improved rate and cycling performance for Si-based anodes.[8] Currently, various prelithiation methods (e.g., prelithiation additives, direct contact methods, Li-containing complex solution, and electrochemical cycling) have been reported. Although these strategies could all achieve Li compensation in the batteries, their universality and feasibility in practical applications vary greatly, which pose enormous challenges for large-scale applications. Therefore, a practical evaluation is required to accelerate the realization of effective prelithiation in industry.

Herein, we systematically summarize the development of various prelithiation strategies according to different steps in the commercial battery manufacture procedure, which can be roughly divided into the following: (1) active material synthesis, (2) slurry mixing process, (3) electrode pretreatment, and (4) battery fabrication (Figure 1). Moreover, the advantages and challenges of these prelithiation strategies will be evaluated in terms of various aspects including accuracy, economy, convenience, uniformity, prelithiation capacity, and safety during large-scale production. This review aims to provide an in-depth understanding of the future development of prelithiation strategies toward commercial and practical applications. At the same time, this work has reference value to the presodiation/prepotassiation toward high-performance sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs).

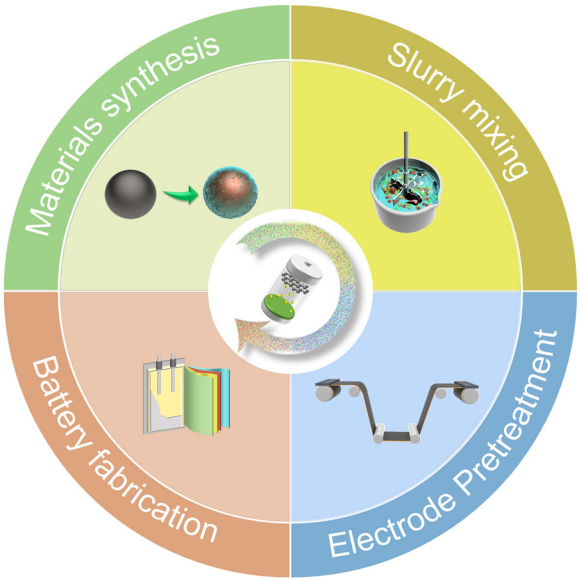

FIGURE 1 Schematic illustration of the prelithiation strategies in the different steps for the commercial battery manufacture procedure

2 | PRELITHIATION DURING MATERIAL SYNTHESIS

Since the intrinsic properties of active materials directly determine the battery performance, prelithiation during material synthesis is a widely adopted method to directly compensate for ICL. Prelithiation of this process can be divided into two categories: (1) modification of active material with lithium-containing compound by means of coating or filling and (2) conversion of lithium-free or lithium-deficient active materials into lithiated species via bulk phase transformation.

2.1 | Surface prelithiation

Apart from low ICE, the large volume swing of Si-based materials during cycling induces unstable SEI, resulting in subsequent capacity loss. By combining mechanical mixing with low-temperature heat treatment, lithium stearate can be filled into the pores and defects of a silicon nano alloy (SiNA), while forming a protective SEI on the surface (Figure 2A). The introduction of lithium stearate leads to partial prelithiation of SiNA and simultaneously enhances the mechanical strength and

toughness of SiNA active material,[9] showing significant improvement in both Coulombic efficiency and cycle performance. In addition, Guo et al. used lithium carbonate (Li_2CO_3), polyacryl alcohol (PVA), and pitch as supporting raw materials, to form lithium silicate (Li_2SiO_3), a main irreversible phase generated during the initial lithiation process, on the surface of silicon monoxide active particles by the annealing process (Figure 2B).[10] Consequently, the ICE of the prelithiated SiO composite anode with the preformed lithium silicate shield was improved.

Qian et al. used $LiBH_4$ as the prelithiation reagent to construct an artificial SEI film (Li_2SiO_3) on the surface of a Si anode by thermal treatment processes in different atmospheres, resulting in the strengthening of electrode integrity and improvement of the ICE of the Si anode half-cell and full-cell.[13] Furthermore, the SnO_2 anode was wrapped with LiF using a ball-milling process (Figure 2C).[11] The LiF passivation layer not only provides additional active Li^+ but also suppresses the decomposition of the electrolyte, which has a positive effect in improving the reversible capacity. In addition, LiF can maintain the stability of the composite material structure, based on the strong interaction of F–Sn, F–O, and F–C bonds.

In addition to modifying anode materials, interfacial reconstruction on cathode materials is also a possible approach. Sun et al. soaked $LiCoO_2$ cathode material in a Li-naphthalene (NP)/tetrahydrofuran (THF) solution to form a Li_2O/Co nanoshell on the surface of $LiCoO_2$ particles (Figure 2D).[12] The Li_2O/Co shell donates additional active Li^+ through the conversion reaction ($4Li_2O + 3Co \rightarrow 8Li^+ + 8e^- + Co_3O_4$) during the initial charge, which can reduce the ICL of the anode. The thickness of the Li_2O/Co shell can be regulated by adjusting the ratio of Li–NP to $LiCoO_2$, thereby achieving precise control over the degree of prelithiation.

2.2 | Bulk prelithiation

Apart from surficial modifications, prelithiation can also be achieved in the bulk of active materials. For Si-based materials, Sakaguchi et al. prepared a prelithiated Li_xSi alloy by ball-milling Si particles with lithium chips under Ar for prelithiation and it showed 1.5 times longer cycle

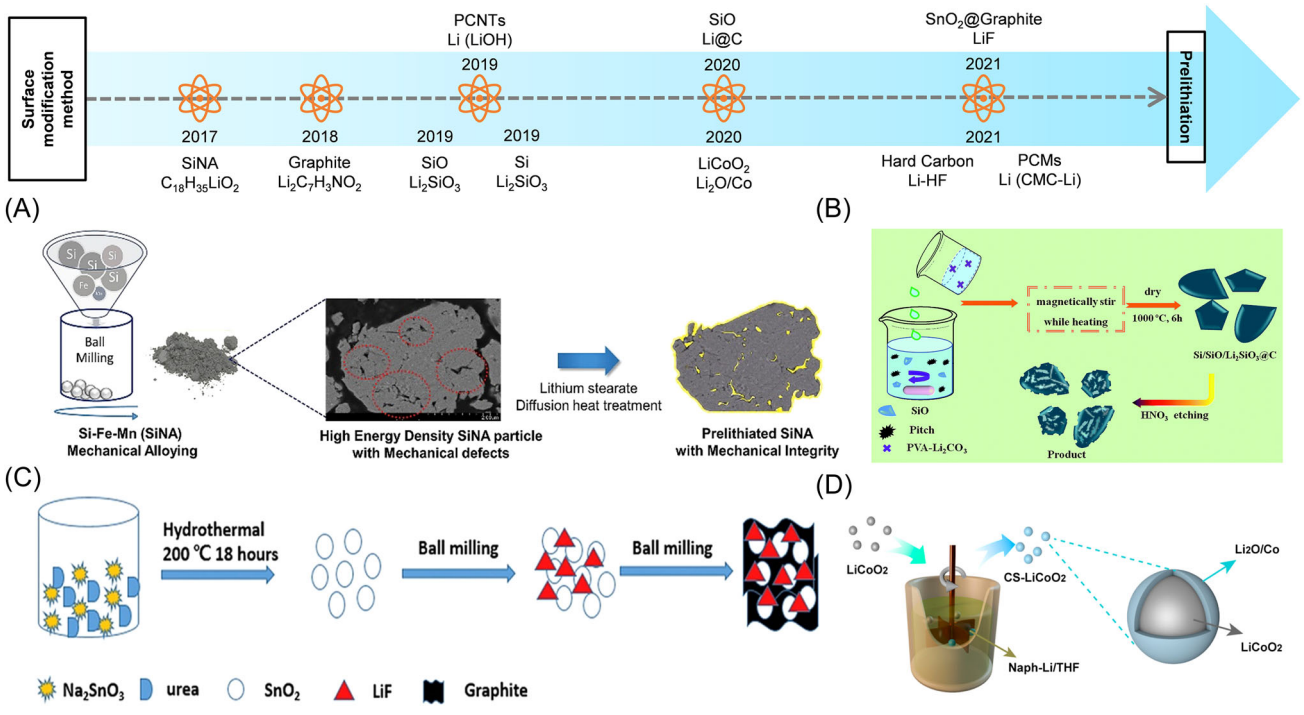

FIGURE 2 Representative studies on the surface prelithiation method. (A) Schematic prelithiation procedures of SiNA via mechanical mixing and low-temperature heat treatment. Reproduced with permission: Copyright 2017, Elsevier.[9] (B) Schematic synthesis procedures of the Si/SiO/Li_2SiO_3@C composites via a facile method using SiO, pitch powder, and Li_2CO_3–PVA, solution followed by annealing treatment. Reproduced with permission: Copyright 2019, Royal Society of Chemistry.[10] (C) Schematic of LiF@SnO_2@C nanosheets using the ball-milling method. Reproduced with permission: Copyright 2021, Elsevier.[11] (D) Schematic illustration of the preparation of a Li_2O/Co nanoshell-coated $LiCoO_2$ by a chemical reaction between Li-NP and $LiCoO_2$. Reproduced with permission: Copyright 2020, American Chemical Society.[12]

life than a pristine Si anode.[14] In addition, prelithiation of the SiO anode can be achieved by heating a mixture of SiO/SiO_2 and lithium powders under an argon atmosphere, generating irreversible phases (Li_2SiO_3, Li_4SiO_4, Li_2O),[15] which could be regulated by changing the heating rate and temperature. The above-mentioned prelithiation method for Si-based materials has already been commercialized and could increase the ICE above 90%. To tackled severe volume expansion of Si-based materials, amorphous TiO_2-encapsulated silicon nanoparticles were chosen and mixed with molten lithium metal to obtain a Li_xSi-Li_2O/Ti_yO_z composite anode (Figure 3A).[16] The prelithiated TiO_2 protective layer (Li_2O/Ti_yO_z) reduces the ICL by limiting the formation of SEI, improves the stability of the active material in dry air, and enhances the conductivity of the active material due to the formation of oxygen vacancies. Alternatively, as another method of commercialization, premagnesization treatment of Si-based materials can also lead to improvements in the ICE and cycling performance. Recently, Fang et al. achieved a capacity retention of 91% after 200 cycles for a Si anode using Li_xMg and LiH.[23] Lee et al. prepared a $SiO_x/Mg_2SiO_4/SiO_x$ composite by a simple combination of the magnesiothermic reduction process and acid treatment, which effectively improves the ICE (from 56.6% to 75.6%) and prevents volume expansion.[24]

In addition to using lithium metal as the lithium source, other lithium-containing compounds, such as LiH,[17] have also been developed for prelithiation of Si-based materials (Figure 3B). Prelithiation of SiO with LiH thermal dehydrogenation not only results in the preformation of Li_2SiO_3 to improve the ICE of SiO (from 59.3% to 90.5%), but the generated hydrogen also facilitates a 3D network structure, which mitigates the volume expansion of Si-based materials. Furthermore, a novel chemical prelithiation strategy was adopted by Guo and coworkers to obtain uniformly distributed Li_xSiO_y inside the Si-based particles (Figure 3C).[18] By calcining the SiO_x/C material prelithiated by lithium-biphenyl/tetrahydrofuran (Li-BP/THF) solution at a high temperature, a homogeneous Li_xSiO_y distribution in the bulk of SiO_x can be achieved. Additionally, Kim et al. used a Li-BP derivative, that is, lithium-4,4′-di-tertbutyl biphenyl (Li-DTBP), to simultaneously achieve prelithiation and reduction of graphene oxide (GO) active materials using ultrasound (Figure 3D).[19] The prelithiation process induced the formation of an SEI composed of lithium carbides and lithium compounds, which promotes the charge transfer and Li^+ diffusion of the GO material. Using the same method, Sun et al. obtained layered lithium-rich $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ (LR-Ni65) cathode material using a Li-NP/THF solution (Figure 3E).[20] In addition to the higher ICE, the formed LR-Ni65 shows enhanced cycling stability due to the regulation of the Li/Ni disorder. Also, Chen et al. constructed a galvanic cell to prelithiate SnO_2 with metallic lithium as the lithium source.[25] Recently, Singh et al. directly integrated prelithiation and material synthesis to prepare prelithiated $ZnMoO_4$, which showed better reversible capacity (~1000 mAh g^{-1} at 0.1 A g^{-1}) and superior rate capability (~400 mAh g^{-1} at 2 A g^{-1}).[26]

A spinel-type $LiMn_2O_4$ cathode can store extra irreversible Li^+ with the help of the Mn^{4+}/Mn^{3+} redox pair, thereby forming a Li-rich $Li_{1+x}Mn_2O_4$ ($0 < x < 1$) phase.[27] The irreversible Li^+ in $Li_{1+x}Mn_2O_4$ can be released during the first cycle, so prelithiation of the spinel $LiMn_2O_4$ cathode is a feasible method to compensate for the anodic ICL in a full battery. As early as 1991, Tarascon et al. prepared $Li_2Mn_2O_4$ by heating a vacuum-encapsulated mixture of $LiMn_2O_4$ and LiI.[28] After that, Abrahom et al. successfully prepared Li-rich $Li_{1+x}Mn_2O_4$ using a normal-butyllithium (n-BuLi)/hexane solution.[29] However, the potential safety risk linked to the use of n-BuLi reagent and the long duration of the prelithiation process are not suitable for industrial applications; hence, it is necessary to explore a more suitable prelithiation method.

With a much higher working potential (> 4.5 V vs. Li^+/Li) compared with $LiMn_2O_4$ (4 V vs. Li^+/Li), $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is another promising spinel cathode material.[21,30] Manthiram et al. applied inexpensive tetraethylene glycol (TEG) and hydrated LiOH to convert the LNMO spinel phase into a lithium-rich $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ (LLNMO, $0 < x < 1$) phase in an ambient environment via microwave heating (Figure 3F).[21] Furthermore, Margret et al. prepared the LLNMO phase by low-temperature thermal treatment of a mixture of LNMO and LiOH in a reductive condition. Lithium and ammonia can form a strong reducing reagent to reduce manganese and chemically lithiate the active material. The obtained LLNMO showed high capacity and Coulombic efficiency in full-cells.[31,32] Similarly, Johnson et al. successfully prepared lithium-rich LLNMO using liquid ammonia and metallic lithium as reactive agents, which increases the reversible capacity of the full-cell (Si-Gr as anode) by 23%.[33] However, due to the utilization of liquid ammonia, this reaction needs to be carried out under relatively complex and harsh conditions (high pressure, low temperature). To achieve more scalable prelithiation, this strategy was improved by Schmuch et al. by replacing liquid ammonia with 1-pentanol (Figure 3G),[22] which allows the prelithiation reaction to take place under a milder condition.

Compared with the use of prelithiation agents to lithiate the as-prepared active materials, integration of the prelithiation step into the synthesis simplifies the

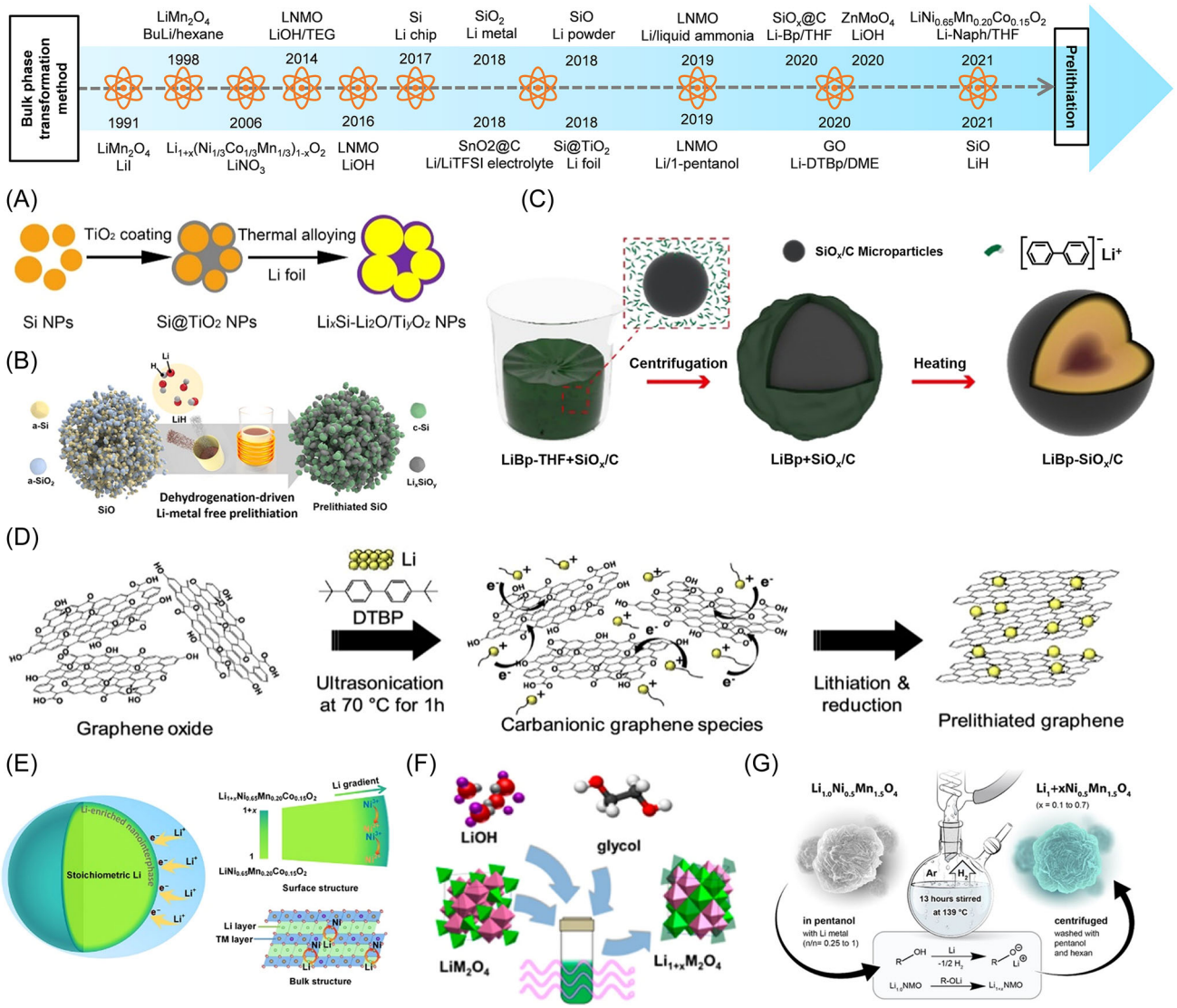

FIGURE 3 Representative studies on bulk prelithiation methods. (A) Schematic of the fabrication process for Li_xSi-Li_2O/Ti_yO_z core–shell NPs using a coating-then-alloying approach. Reproduced with permission: Copyright 2018, American Chemical Society.[16] (B) Schematic illustration of the phase transformation for SiO by dehydrogenation-driven Li metal-free prelithiation. Reproduced with permission: Copyright 2021, Elsevier.[17] (C) Schematic illustration of the prelithiation process for the SiO_x/C via chemical reaction in Li-BP/THF solution and heat treatment. Reproduced with permission: Copyright 2020, American Chemical Society.[18] (D) Schematic illustration of the synthesis of prelithiated graphene by chemical reaction between GO and Li-DTBP using ultrasound. Reproduced with permission: Copyright 2020, American Chemical Society.[19] (E) Schematic illustration of the lithium-enriched gradient interphase layer-coated $LiNi_{0.65}Mn_{0.20}Co_{0.15}O_2$ cathode with partial Li/Ni disorder. Reproduced with permission: Copyright 2021, American Chemical Society.[20] (F) Schematic illustration of the synthesis of $Li_{1+x}M_2O_4$ (M = Mn, Ni) using LiOH, glycol, and LiM_2O_4 under microwave heating conditions. Reproduced with permission: Copyright 2014, American Chemical Society.[21] (G) Schematic illustration of the synthesis of prelithiated $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ via stirring $Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$ with Li in boiling pentanol. Reproduced with permission: Copyright 2019, Electrochemical Society.[22]

preparation procedure. For instance, overlithiated $Li_{1+x}(Ni_zCo_{1-2z}Mn_z)_{1-x}O_2$[34] and $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O_2$[35] were synthesized using the spray-drying method, overlithiated $Li_{1+x}Ni_{0.8}Co_{0.2}O_2$[36] was synthesized using the combustion/annealing method, and lithium-rich $xLi_2MnO_3{\cdot}(1-x)Li[Mn_yNi_zCo_{1-y-z}]O_2$[37] was synthesized using the co-precipitation method.

In brief, the prelithiated active materials prepared using the principle of bulk phase transition are effective in reducing ICL. Also, the prelithiation level can be regulated by varying the ratio of prelithiation reagents to active materials, prelithiation time, heating rate, and annealing temperature. However, the current mainstream lithium sources (e.g., LiH) are sensitive to

the ambient atmosphere, and the preparation conditions of the materials are relatively harsh (e.g., inert atmosphere and high temperature). Therefore, from the perspective of cost, safety, and scalability, it is necessary to seek suitable prelithiation reagents and improve synthesis methods for commercialization.

3 | PRELITHIATION DURING SLURRY MIXING

During the slurry mixing process, prelithiation reagents are introduced into the electrode as additives. Ideally, the prelithiation reagents should have the following properties: (1) high irreversible capacity; (2) suitable reaction voltage, that is, specifically, the delithiation/lithiation potential of the cathode additive should be lower than the maximum/minimum cut-off potential of traditional cathode materials and the redox potential of the anode additive should also be lower than the lithiation potential of the anode material; and (3) satisfactory chemical stability, that is, prelithiation agents should remain stable during slurry preparation.

3.1 | Anode prelithiation additive

For the anode prelithiation additive, as the electrolyte wets the anode-containing additive, a short circuit is formed between the additive and the active material, leading to spontaneous lithiation or SEI-formation reactions. At present, the most representative prelithiation reagent is Li_xSi nanoparticles with ultrahigh prelithiation capacity (above 1200 mAh g^{-1}) and a low delithiation voltage (about 0.4 V). Moreover, the preparation of Li_xSi nanoparticles is simple; they can be synthesized by a solid-phase reaction using Si-based nanoparticles and lithium metal as raw materials under an inert gas atmosphere. When a small amount of Li_xSi was added to Si-, graphite-, and Sn-based anodes, the improvement of ICE was significant.[38–40] For example, Li_xSi–Li_2O core–shell nanoparticles synthesized from nano-silicon by Cui et al. not only showed a high prelithiation capacity of 1310 mAh g^{-1} but also maintained 91% of the capacity after one day of storage in dry air (Figure 4A).[39] However, when Li_xSi–Li_2O core–shell nanoparticles were exposed to moisture-laden air, their capacity decreased markedly. To enhance the resistance of Li_xSi to moisture, they treated Li_xSi nanoparticles with a nonpolar 1-fluorodecane/cyclohexane solution, thereby constructing a layer of continuous and dense artificial SEI composed of LiF and lithium alkyl carbonate with long hydrophobic carbon chains on the surface, which results in a capacity of 1604 mAh g^{-1} (corresponding to 76% of the initial capacity) after storage in air at a relative humidity (RH) of 10% for 6 h.[38] Li_xSi/Li_2O composites obtained by replacing nano-silicon with SiO or SiO_2 showed superior ambient environment compatibility (1240 mAh g^{-1} capacity after 6 h of exposure to 40% RH).[40] In the Li_xSi/Li_2O composite structure, the Li_xSi nanodomains are uniformly distributed in the crystalline Li_2O matrix, resulting in a huge contact area between Li_xSi and Li_2O (Figure 4B). According to density functional theory (DFT) theoretical calculations, there is a strong interaction between the oxygen atom in Li_2O and the lithium atom in Li_xSi, which effectively stabilizes lithium atoms in Li_xSi. Therefore, compared with the core–shell Li_xSi–Li_2O composite, the Li_xSi/Li_2O composite shows improved ambient stability. Inspired by the excellent prelithiation ability of Li_xSi nanoalloys, Li_xZ alloys and Li_xZ–Li_2O composites (Z = Ge, Sn, etc.) were also synthesized in similar ways as anode prelithiation additives.[41] Among all Li_xZ alloys, the Li_xGe alloy has the best ambient stability (negligible capacity fading of 6.5% in dry air for 5 days) due to the largest binding energy between Li and Ge in the $Li_{22}Ge_5$ crystal (Figure 4C). However, Li_xZ reacts violently with highly polar solvents (organic carbonates, N-methylpyrrolidon (NMP), etc.),[38–41] making them incompatible with industrial slurry processes.

For better compatibility of anode prelithiation additives with the NMP solvent, Chen et al. treated a lithium carbon (Li–C) microsphere composite prelithiation additive with octade-cylphosphonic acid (OPA) to obtain a self-assembled monolayer (SAM) passivation layer on the surface.[42] The passivation layer not only effectively inhibits the reaction between the prelithiation active material and the NMP solvent but also improves the ambient stability of the prelithiation active material (Figure 4D), showing satisfactory industrial processing compatibility. Therefore, this modification strategy may be extended to Li_xZ prelithiation additives.

Because of high irreversible capacity from decomposition (about 800 mAh g^{-1}) and low delithiation potential (about 1.0 V),[43,44] $Li_{2.6}Co_{0.4}N$ is considered a promising anode prelithiation reagent that can well compensate anodic ICL. By introducing $Li_{2.6}Co_{0.4}N$ into SnO and $SiO_{1.1}$ anode materials, Yamamoto et al. obtained much-improved ICE in both SnO (from 44% to 86%)[45] and $SiO_{1.1}$ (from 49% to 95%).[46] Furthermore, mixing of $Li_{2.6}Co_{0.4}N$ with a Si–Gr composite,[47] HC,[48] and Gr[49] active particles is also found to effectively improve their ICEs.

3.2 | Cathode prelithiation additive

Li-containing cathode additives are oxidized during the initial charging process, so their oxidation voltages should fall within the working potential window of the chosen cathode material.

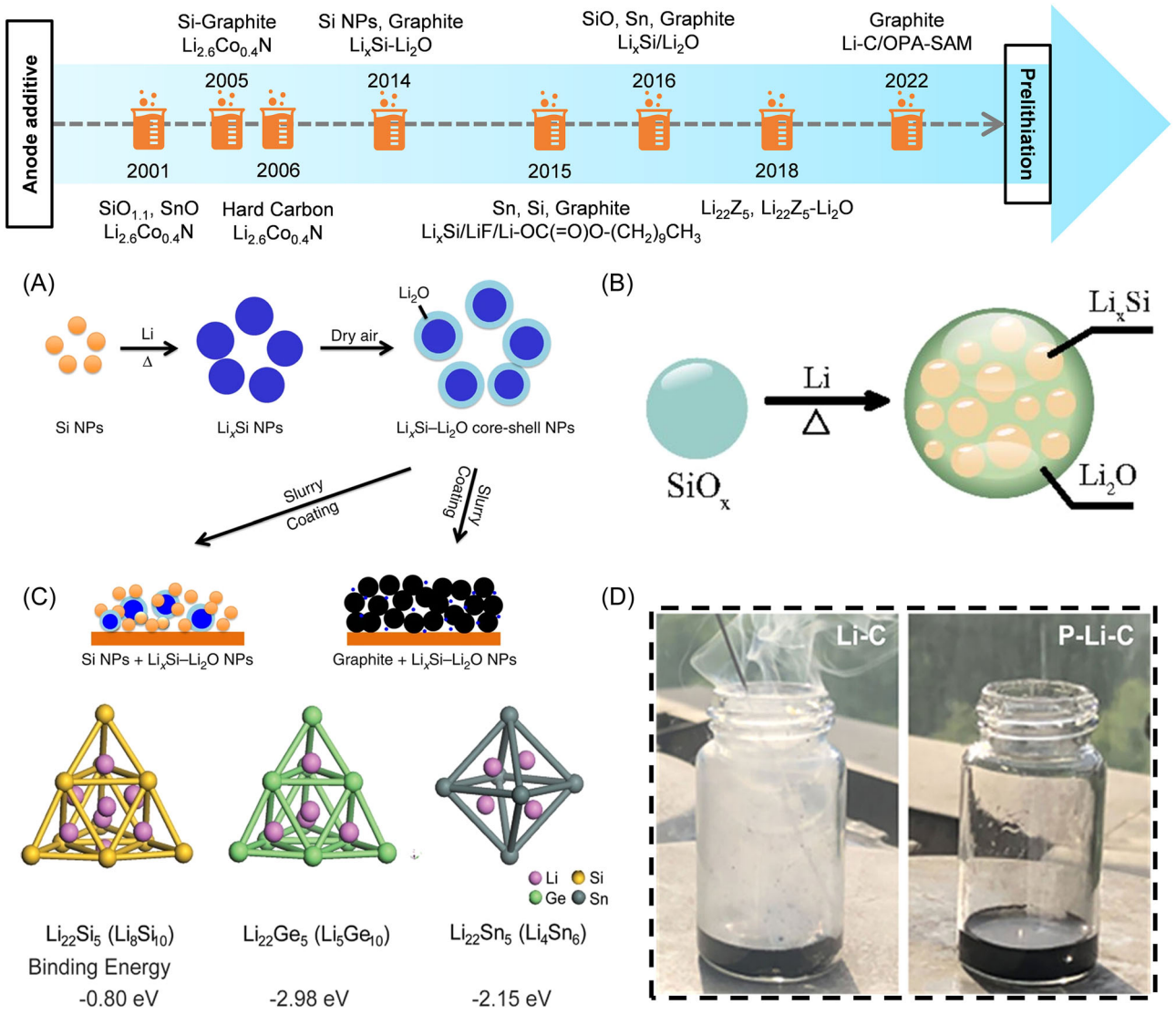

FIGURE 4 Representative studies on anode prelithiation additives. (A) Schematic diagrams showing that Si NPs react with melted Li to form Li_xSi NPs. Reproduced with permission: Copyright 2014, Springer Nature.[39] (B) Schematic illustration of the synthesis process for the Li_xSi/Li_2O composite by a chemical reaction between SiO_x and Li. Reproduced with permission: Copyright 2016, National Academy of Sciences.[40] (C) The binding energy of Li with Z (Z = Si, Ge, and Sn). Reproduced with permission: Copyright 2018, Elsevier.[41] (D) The image comparison of Li–C and P–Li–C soaked in NMP in the ambient atmosphere. Reproduced with permission: Copyright 2022, Wiley.[42]

As a typical category of prelithiation additives, lithium-rich transition-metal oxides are usually stable in NMP solvents, showing good industrial feasibility. In 2000, Koksbang et al. proposed spinel lithium-rich manganese-based materials as cathode prelithiation additives.[50] Subsequently, Li_2CuO_2[51] and Li_2NiO_2[52–54] were developed as prelithiation additives for $LiMn_2O_4$ and $LiCoO_2$ cathodes, respectively. Although Li_2NiO_2 has a higher capacity than Li_2CuO_2, Li_2CuO_2 is completely stable in air, while Li_2NiO_2 is sensitive to moisture, which is unfavorable for industrial production. To make up for this shortcoming of Li_2NiO_2, Al_2O_3-coated Li_2NiO_2 was successfully prepared through the reaction of Al iso-propoxide with Li_2NiO_2.[55] The Al_2O_3 protective layer significantly improved the ambient stability of Li_2NiO_2. Anti-fluorite-type materials are also a viable class of cathode prelithiation additive materials. With high capacity (greater than 600 mAh g^{-1}) and suitable de-lithiation potential (3.5–4.0 V), Li_5FeO_4 (LFO) showed excellent prelithiation ability as a cathode additive.[56–60] Lu et al. added 7 wt% LFO to the $LiCoO_2$ cathode to increase the reversible capacity of the $LiCoO_2$||HC full-cell from 126 to 144 mAh g^{-1}, resulting in a significant increase in energy density.[61] To improve the electronic conductivity of LFO and lower its charging potential, Kim et al. used an Fe_3O_4/CNT nanocomposite as the raw material to prepare LFO/CNT composites.[60] Moreover, it should be mentioned that LFO is also sensitive

to moisture,[59] which poses a challenge for slurry mixing as well as subsequent processes. Similar to LFO, Li_6CoO_4 is a lithium-rich material with an anti-fluorite structure.[62,63] According to the DFT theoretical calculation and experimental characterization, Li_6CoO_4 would preferentially undergo topological phase transition during the charging process, accompanied by the extraction of two Li^+. The resultant Li_4CoO_4 phase would continuously decompose into Li_2O and CoO_2, delivering a capacity as high as ~1000 mAh g^{-1}.[62] Hence, Cho et al. added 15 wt% Li_6CoO_4 as a cathode additive to the $LiCoO_2$||SiO_x full-cell and achieved an enhancement of discharge capacity from 77 to 133 mAh g^{-1}.[63]

Apart from Li-containing transition-metal oxides, some lithiating compounds will decompose into Li^+ and gases during the first charging process without leaving extra "dead weight" in the electrode. Those compounds usually have higher capacity and stronger prelithiation ability than lithium-rich transition-metal oxides, including Li_3N (2308.5 mAh g^{-1}),[64] Li_2O (1675 mAh g^{-1}),[65] Li_2O_2 (1168 mAh g^{-1}),[66] and so forth. In 2010, Armand et al. first proposed LiN_3 as a positive sacrificial salt to compensate for the ICL of an anode.[67] However, the toxicity of LiN_3 limits its large-scale application and research. As an alternative to LiN_3, Li_3N is safer and has much higher capacity; thus, it is more suitable as a cathode prelithiation additive. Nevertheless, Li_3N only stably exists in dry air[64] and it is not compatible with NMP.[68] To tackle these issues, Cui et al. constructed a dense passivation layer composed of Li_2O and Li_2CO_3 on the surface of Li_3N by annealing,[68] and similarly, Chen et al. directly aged Li_3N in dry air to obtain a Li_2CO_3 coating.[69] Compared with Li_3N, Li_2O is highly compatible with NMP and has a higher theoretical capacity (1675 mAh g^{-1}), making it a favorable candidate as a prelithiation additive for a number of cathodes.[65,70] Unfortunately, Li_2O also readily reacts with moisture to form LiOH, resulting in poor ambient tolerance. To circumvent this shortcoming, Johnson et al. introduced a Co_3O_4 coating onto the Li_2O surface by ball milling.[70] As a promising additive, Li_2O_2 has low conductivity, leading to a decomposition capacity of 171.1 mAh g^{-1} at 4.6 V versus Li/Li^+, which is much lower than the theoretical value. When coupled with the $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM) cathode, a charging capacity of 1109.1 mAh g^{-1} (without the contribution of NCM) can be achieved, showing a voltage plateau at 4.2–4.3 V.[66] It is revealed that NCM acts as a catalyst to reduce the overpotential of Li_2O_2 activation and promote the decomposition of Li_2O_2. As with Li_2O_2, the decomposition voltage of $Li_2C_2O_4$ is high (about 4.7 V), which is too high for commercial cathode materials.[71] This challenge can be addressed by optimization of the substituents on the carbon chain. According to the cross verification of DFT theoretical calculation and experimental results, the decomposition voltage of organic metal carboxylates is directly related to the strength (binding energy) of the oxygen–metal (O–M, M = Li, Na, K) moiety. The stronger the electron-donating effect of the substituent, the weaker the O–M binding energy, and the lower the decomposition voltage (Figure 5A).[72] Furthermore, the O–M binding energy is also directly related to the charge density of the cation. The low charge density can reduce the decomposition voltage of O–M. In addition to LIBs, these organic metal carboxylates have been expanded to presodiation of SIBs and prepotassiation of PIBs.

Alternatively, transition metals (Fe, Co, Ni, etc.) are added to sacrificial lithium compounds (LiF, Li_2S, Li_2O, etc.) to form conversion-type nanocomposites.[70,75–78] Usually, they can be obtained simply by mechanical mixing of transition-metal compounds and molten lithium metal via a one-step simple solid-phase reaction in an inert gas atmosphere (Figure 5B,C).[74,76,78] As catalysts with inherent conductivity, transition metals could greatly reduce the decomposition overpotential of lithium compounds, promoting electrochemical decomposition. Despite the relatively lower capacity compared with pure sacrificial lithium compounds, these nanocomposites enable more efficient prelithiation. Furthermore, these nanocomposites can coexist well with polyvinylidene difluoride (PVDF) and NMP, which can be scaled up for industrial production. At present, the main nanocomposite prelithiation additives include LiF/Co (516 mAh g^{-1}),[73] LiF/Fe (506 mAh g^{-1}),[73] Li_2S/Co (670 mAh g^{-1}),[78] Li_2S/Fe (480 mAh g^{-1}),[78] Li_2O/Co (609 mAh g^{-1}),[74] Li_2O/Fe (612 mAh g^{-1}),[74] Li_2O/Ni (495 mAh g^{-1}),[74] and so on. Adding these prelithiation species to the cathode can effectively improve the first-cycle charge capacity and compensate for the ICL of the anode. For instance, the charge capacity of $LiFePO_4$ with a 4.8% Li_2S/Co additive increases by 42 mAh g^{-1} in the first cycle.[78] In addition to the above nanocomposites, Sun et al. prepared a new type of Fe/LiF/Li_2O nanocomposite by the solid-phase reaction between FeOF powder and lithium metal (Figure 5D), which combines the stability of LiF/Fe with the high capacity of Li_2O/Fe.[75] As a consequence, the nanocomposite showed acceptable environmental stability (retaining 65% of capacity when exposed to air with 20% RH for 2 days) and excellent prelithiation capability (527 mAh g^{-1}). Since the release of Li^+ in these nanocomposites is achieved by the inverse conversion reaction between lithium compounds and transition metals, good contact between the two reactants is crucial. To form a

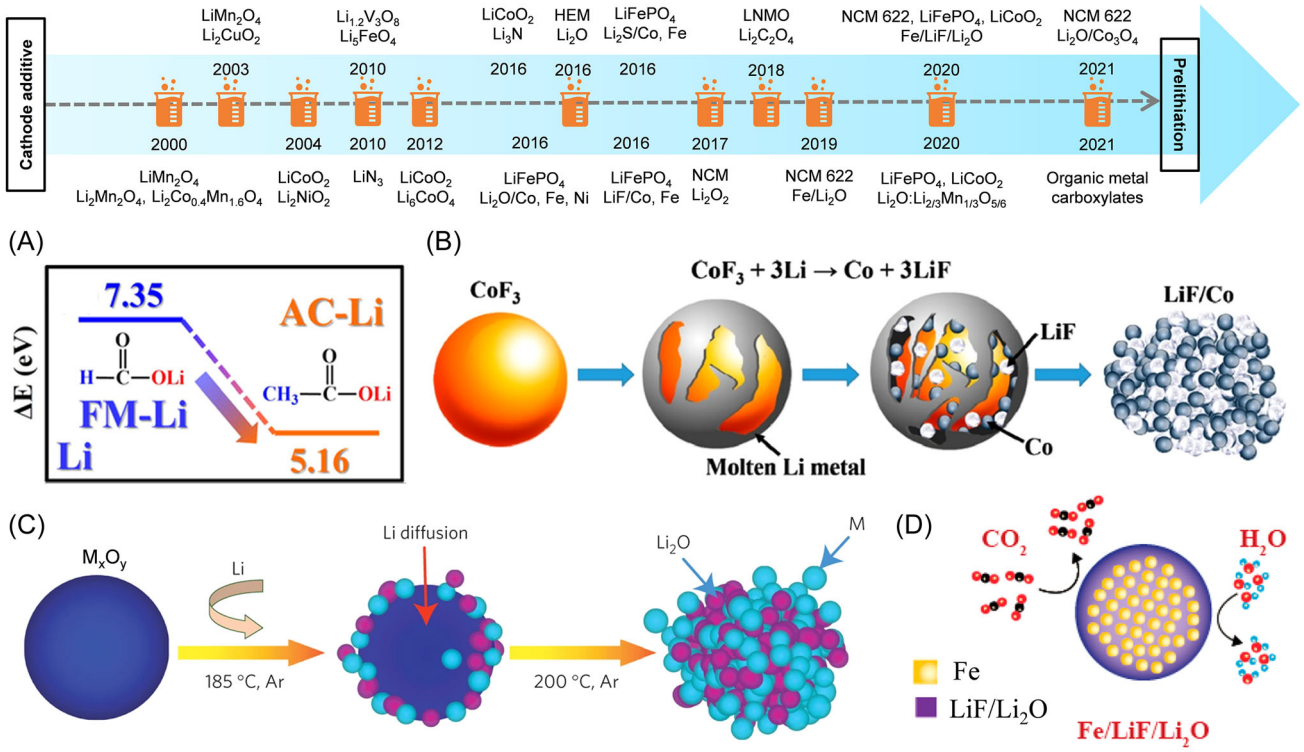

FIGURE 5 Representative studies on cathode prelithiation additives. (A) Variation tendency of O–Li bonding energy in the lithium carboxylate system with different substituents. Reproduced with permission: Copyright 2021, Wiley.[72] (B) Schematic of the formation process of LiF/Co nanocomposite via a chemical reaction between CoF_3 and Li. Reproduced with permission: Copyright 2016, American Chemical Society.[73] (C) Schematic of the fabrication process of Li_2O/M (M = Fe, Co, Ni) nanocomposites via chemical reaction between M_xO_y and Li. Reproduced with permission: Copyright 2016, Springer Nature.[74] (D) Chemical stability of Fe/LiF/Li_2O nanocomposites in ambient air. Reproduced with permission: Copyright 2020, American Chemical Society.[75]

more homogeneous composite, Qiu et al. used Li_2CO_3/C composites and $FeC_2O_4{\cdot}2H_2O$ as raw materials to prepare Fe/Li_2O nanocomposites by calcination in vacuum.[77] In the structure of the composite prepared using the solid-phase synthesis method, the lithium compound nanodomains are uniformly distributed in the metal matrix, providing many contact areas between them, which is favorable for the electrolytic delithiation reaction.

Although both anode additives and cathode additives can significantly decrease the ICL of anode, they also have some shortcomings. With high chemical reactivity, anode prelithiation reagents are sensitive to moisture and polar solvents (NMP, organic carbonates), resulting in poor compatibility with industrial processing. For cathode additives, lithium-rich transition-metal oxides and conversion-type nanocomposites produce inert transition-metal oxides after the first charge, which negatively affects battery energy density. Lithium-rich transition-metal oxides and sacrificial lithium compounds show high delithiation potential, which may induce oxidative decomposition of the electrolyte. Apart from poor viability in ambient conditions and NMP solvent, the decomposition of sacrificial lithium compounds also generates extra gases, which potentially increases the safety hazard during the battery formation manufacturing process. In addition, the utilization efficiency of the cathode and anode prelithiation additives is also an issue that needs to be considered as current reports rarely focus on this aspect.

4 | PRELITHIATION DURING THE ELECTRODE PRETREATMENT

4.1 | Direct contact with lithium metal

Due to the low potential (−3.04 V vs. SHE), Li metal in various states, such as a Li foil and stabilized Li metal powders (SLMP), is able to chemically reduce anode materials, accompanied by the insertion of Li^+. Recently, it has been reported that various anode materials, such as Gr,[2,79,80] HC,[2,81] porous carbon-Fe_3O_4,[82] Si-based anodes,[83–91] and carbon nanotube film,[92,93] and so forth, could be prelithiated by direct contact with a Li foil in

the electrolyte. For example, Cui et al. prelithiated a silicon nanowire (SiNW) anode by a facile self-discharge mechanism (Figure 6A).[89] SiNWs grown on stainless steel were directly attached to a Li foil under pressure induction in the electrolyte, which resulted in ~2000 mAh g^{-1} of lithium preloaded for 20 min prelithiation. It is also revealed that the lithiation occurs preferentially not only in smaller Si particles but also on the surface directly in contact with Li (Figure 6B).[88] By default, using the prelithiation method through direct contact with the Li foil, it is difficult to accurately tune the prelithiation rate, uniformity, and degree. However, if the direct contact method has an external circuit and separator, the prelithiation process can be regulated by adding a resistor or a voltmeter. Choi et al. controlled the degree of prelithiation by monitoring the voltage between the anode and the lithium foil.[94] Also, it is expected to be compatible with the existing roll-to-roll process.

To achieve homogeneous lithiation, Guo et al. further optimized this prelithiation strategy by inserting a resistance buffer layer (RBL) to regulate the Li^+ and electron distribution in the anode interface (Figure 6C).[87] The RBL was assembled by coating poly(vinyl butyral) (PVB) on a carbon nanotube, and the resistance of RBL can be adjusted by regulating the PVB layer. Moreover, the RBL enables good contact between the Li foil and the SiO_x electrode due to its flexible feature, facilitating homogeneous prelithiation. Using a similar strategy, an intermediate buffering layer (IBL) deriving from mesophase pitch that controlled the prelithiation process by modulating the electronic/ionic diffusivities and the contact time was introduced into a Si/Gr composite anode by Ma and coworkers (Figure 6D).[85] As for mass production, the environments (moisture and potential reactive gasses) must be strictly controlled due to the high chemical activity of the lithium foil. To solve this issue, Yang et al. used a polymer coating layer (e.g., poly (methyl methacrylate), PMMA) to preserve Li foil in ambient air.[95] The selected PMMA coating layer is readily soluble in a carbonate-based electrolyte, so anode materials can be in situ lithiated in a cell. This method is also suitable for SIBs and PIBs.

With particle sizes varying from 5 to 50 μm, with SLMP produced by FMC Lithium Co., it is easier to regulate the degree and uniformity of prelithiation.[96,97] It can be manipulated in dry air owing to the presence of a Li_2CO_3 (3 wt%) protection layer (~350 nm). Hence, a pressure activation process is normally required to crack the Li_2CO_3 layer and enables direct contact between the lithium metal and active materials. However, SLMP is not compatible with traditional polar solvents (e.g., NMP and H_2O). To overcome this issue, one effective strategy involves loading SLMP directly onto the surface of the anode. Lee et al. demonstrated an all-solid-state LIB with a specific energy of 225 Wh kg^{-1} based on an SLMP/Si–Ti–Ni composite anode and an FeS/S cathode via cold-pressing for the first time.[98] Besides, prelithiation can also be achieved by coating and crushing SLMP on the surface of the anode. Consequently, the ICE of the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$||SiO full-cell is improved from 48% to 90% owing to the presence of SLMP.[99] Liu et al. revealed that prelithiation with SLMP also promoted stable SEI formation, enhancing the capacity and cycle stability of the Gr anode.[100]

To further improve the uniformity of prelithiation on the anode surface, attempts have been made to disperse SLMP in organic weak polar solvents, such as hexane,[101] toluene,[102,103] p-xylene,[104] and so forth, to form homogeneous SLMP/solvent suspensions, which are dropped or sprayed onto the surface of the electrode. With this strategy, the ICL of HC anodes[2,79,104] and Si-based anodes[101–103] are compensated. Due to the low density of SLMP and the low viscosity of the solvent, it is a challenge to disperse SLMP homogeneously, as SLMP may move away when the solvent evaporates. To solve this problem, Liu et al. introduced a poly(styrene-co-butadiene) rubber (SBR)-PVDF binder to immobilize SLMP into a bulk Gr anode using a dual coating process (Figure 6E).[105] Thereafter, they also developed a simple solution processing method with the mixed binder of SBR and polystyrene (PS) in xylene solvent to achieve uniform dispersion and coating of SLMP.[106] The flexible SBR provided good attachment between the SLMP and the anode surface, while the rigid but brittle PS tends to crack under pressure, enabling the activation process. The uniform SLMP coating can be firmly glued on the anode surface using the traditional casting method, demonstrating potential for industrial production. In addition to SLMP, lithium powder can be prepared using the droplet emulsion technique (DET) method.[107] Huang et al. used the electrochemical plating technique to synthesize air-stable lithium spheres (ASLSs) covered by a LiF/Li_2O protective shell.[108] The superior electrochemical performance of ASLSs is attributed to the small and uniform particle size (0.5–3 μm) and the thinner shell layer (15 nm) compared with the SLMP. As a typical commercial technique, the mentioned advantages of SLMP are listed as follows: (1) the prelithiation degree can be controlled by adjusting the usage of lithium powders; (2) SLMP can be uniformly distributed on the surface of bulk anode; (3) SLMP is stable in dry conditions and is suitable for the present battery production process; and (4) there is no residual lithium metal after prelithiation. However, the large-scale processing of SLMP has potential safety hazards due to its relatively large surface area and high chemical activity.

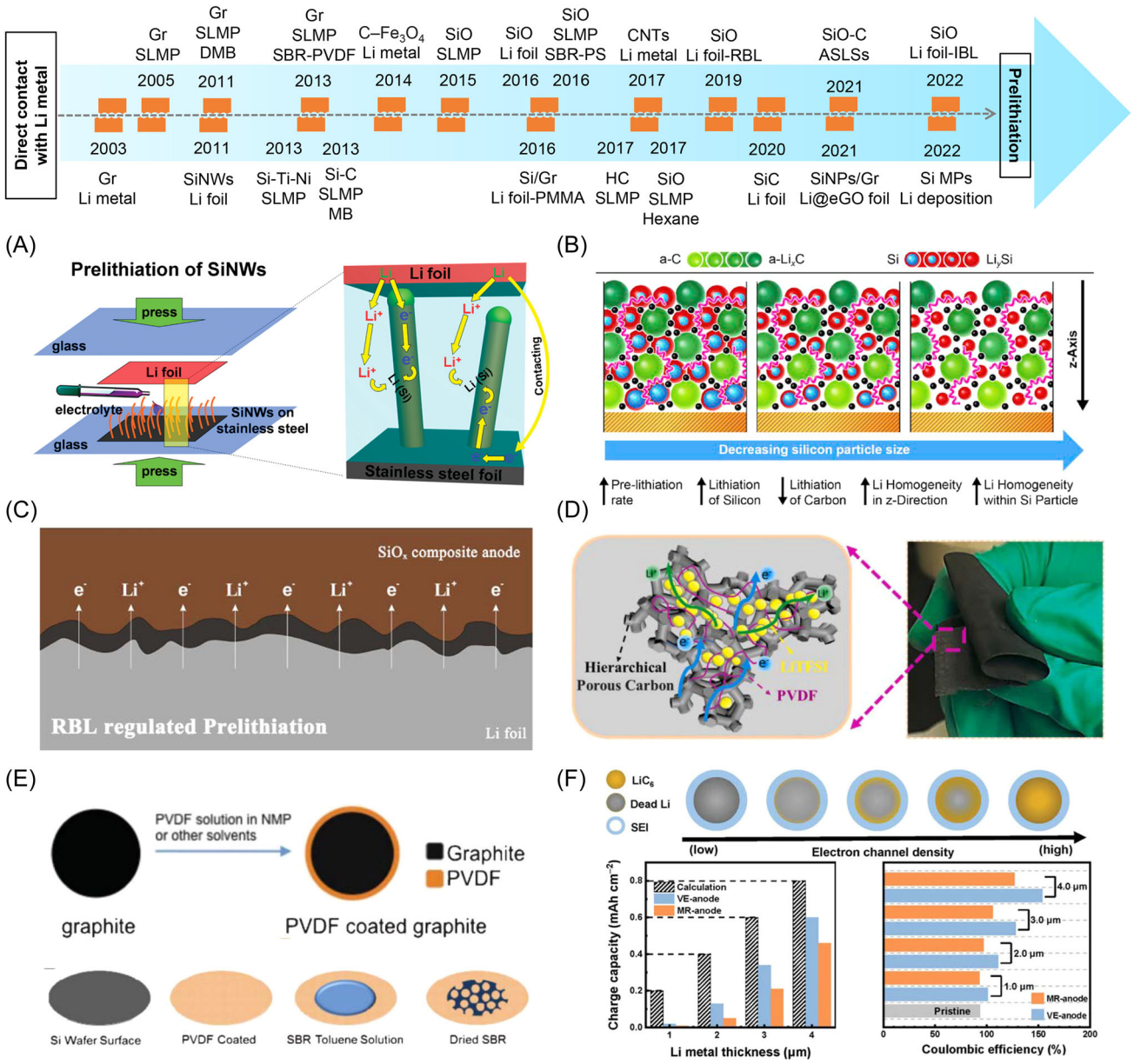

FIGURE 6 Representative studies on prelithiation methods via direct contact with lithium metal. (A) Schematic diagrams of the prelithiation of SiNWs on a stainless-steel foil. Reproduced with permission: Copyright 2011, American Chemical Society.[89] (B) Schematic diagram of the prelithiation behavior in the Si/C composite material. Reproduced with permission: Copyright 2020, Elsevier.[88] (C) Illustration of Li^+ and electron transfer in the RBL-regulated prelithiation process. Reproduced with permission: Copyright 2019, American Chemical Society.[87] (D) Schematic illustration of the ionic/electronic pathways (left) and the optical image of the flexible IBL. Reproduced with permission: Copyright 2022, Elsevier.[85] (E) Schematic illustration of the PVDF–SBR dual coating process. Reproduced with permission: Copyright 2013, Royal Society of Chemistry.[105] (F) Relationship between the electron channel density and the utilization of Li source (above). Comparison of the initial Li-deintercalation capacity and ICE with the MR- and VE-guided contact prelithiation (below). Reproduced with permission: Copyright 2022, Wiley.[84]

Recently, Placke et al. developed a thermal evaporation method for metallic lithium to achieve lithiation of the anode with uniform lateral and in-depth distribution possible.[91] It is also revealed that this process is activated upon the addition of electrolytes. In addition, Zhang et al. constructed different prelithiation interfaces using both mechanical rolling (MR) and vacuum thermal evaporation (VE) methods (Figure 6F).[84] Compared with VE prelithiation, the MR method leads to accumulation of dead Li on the Gr surface, which resulted in considerable polarization and cell degradation. This result is attributed to the promoted prelithiation kinetics enabled by the high mobility of Li steam.

Also, prelithiation can be achieved by coating the electrode surface with Li-rich compounds. Fu et al. deposited Li on the $LiFePO_4$ cathode surface by thermal deposition and synthesized an alpha-Li_3N film under a nitrogen atmosphere.[109] The discharge capacity of the $LiFePO_4$||Gr full-cell increased by 30.7% with 1% Li_3N coating. Moreover, the slurry containing Li_2S could be dropped on the electrode surface to compensate for the loss of active Li due to its high theoretical specific capacity.[110–112]

4.2 | Lithium–organic complex solution prelithiation

In the processes of solution-based chemical prelithiation, a lithium-containing solution with strong reducing ability is used to transfer the active lithium to the active materials through redox reactions. Various solute molecule structures and solvent molecule structures will form different solvation structures, resulting in tunable redox potentials (vs. Li/Li^+). Early in 1998, Owen et al. used 1.6 M n-BuLi hexane solution (~1 V vs. Li/Li^+) to form an SEI layer on the surface of a carbon black anode, which eliminated the ICL. However, the formed SEI is thicker and more brittle than that formed electrochemically, adversely affecting the subsequent cycle performance of the electrode.[113] Later, lithium–arene complex (LAC) solutions were obtained by dissolving NP and lithium metal into solvents of butyl methyl ether (BME),[114] THF,[115] and dimethoxyethane (DME).[116,117] Compared to n-BuLi, the Li–NP complex solution has better chemical stability because its lone pair of electrons is delocalized and distributed on its conjugated aromatic ring (Figure 7A).[117] With the color change of the solution from transparent to dark green, NP radical anions and lithium ions were formed by a spontaneous charge transfer because of NP's electrophilicity, and the solvated lithium ions are doped into the active material. To improve the ICE of the HC anode, Ai et al. applied Li-NP/DME for chemical prelithiation, and they found that a preformed SEI film of the HC anode contains more LiF and organic lithium carbonates than that of the untreated anodes after electrochemical cycling which enables cycling stability (Figure 7B).[116] This might be due to the formation of a dense and robust SEI layer through solution reaction. Meanwhile, this method is also suitable for presodiation in SIBs.[122]

Nevertheless, the redox potential for Li-NP/DME is ~0.35 V versus Li/Li^+, which is higher than the lithiation potential of Si-based anodes (~0.2 V vs. Li/Li^+). Therefore, Li-NP/DME cannot chemically lithiate Si-based anodes but only compensates the ICL of SEI formation. By applying a solvent with stronger electron-donating ability (THF), Minoru et al. decreased the redox potential of the Li-NP LAC (Li-NP/THF), which enabled lithiation in an amorphous Si nano-flake particle anode. Furthermore, by introducing cyano functional groups into NP, the obtained Li-1-cyanonaph-thalene (CNP)/THF solution simultaneously enhanced the ICE and yielded a gradient SEI film with an organic outer layer (dense N-containing organics, $ROCO_2Li$) and an inorganic LiF-enriched inner layer to improve the cycle stability of the SiO anode.[123]

Similar to Li-NP, Li-BP in DME or THF solvents was also used for chemical prelithiation.[118,124,125] Qu et al. introduced a Li-Bp/THF solution to prelithiate a phosphorus/carbon composite electrode, boosting the ICE from 74% to 94% (Figure 7C).[118] Moreover, the solution can be stored in the atmosphere stably for more than 2 weeks, which shows its potential for commercial application. The same strategy was also reported for a prelithiating HC anode[124] and a SnO_2/C nanocomposite anode[125] as well. To achieve the lithium insertion of the Si-based anode, Lee et al. showed that the substituent position of methyl functional groups for BP could reduce the redox potential of Li-BP derivatives,[119] which achieves effective and controllable prelithiation in the SiO_x anode (Figure 7D).

However, the above commonly used prelithiation solvents are incompatible with Gr anode and may undergo a co-intercalation reaction to exfoliate Gr during the prelithiation process. To address this issue, Ai et al. chose 2-methyl tetrahydrofuran (2-Me-THF) as a solvent, which enables accurate prelithiation in Gr anodes without destroying its lattice structure (Figure 7E).[120] Then, Lee and co-workers[121] revealed that LAC solutions with weakly solvating solvents such as 2-MeTHF or tetrahydropyrane (THP) enable the insertion of Li^+ into Gr due to the low Li^+ desolvation energy (Figure 7F). By contrast, solvents with high desolvation energy (e.g., DME and THF) will co-insert into Gr with Li^+, resulting in failure of the subsequent electrochemical cycling.

In short, chemical prelithiation by solution immersion can achieve homogeneous prelithiation, and the degree of lithiation can be manipulated by adjusting the redox potential of complex solution, solution concentration, reaction time, and reaction temperature. The compatibility between the prelithiation reagent and the electrode components (i.e., active material, current collector) should also be considered.[126] Complex solutions with excessive reactivity might destroy the structure of active materials or dissolve the current collector during the soaking process. In addition, increasing the stability in ambient air of these complex solutions is an important issue, and prototype equipment for large-scale roll-to-roll solution chemical prelithiation needs to be designed.

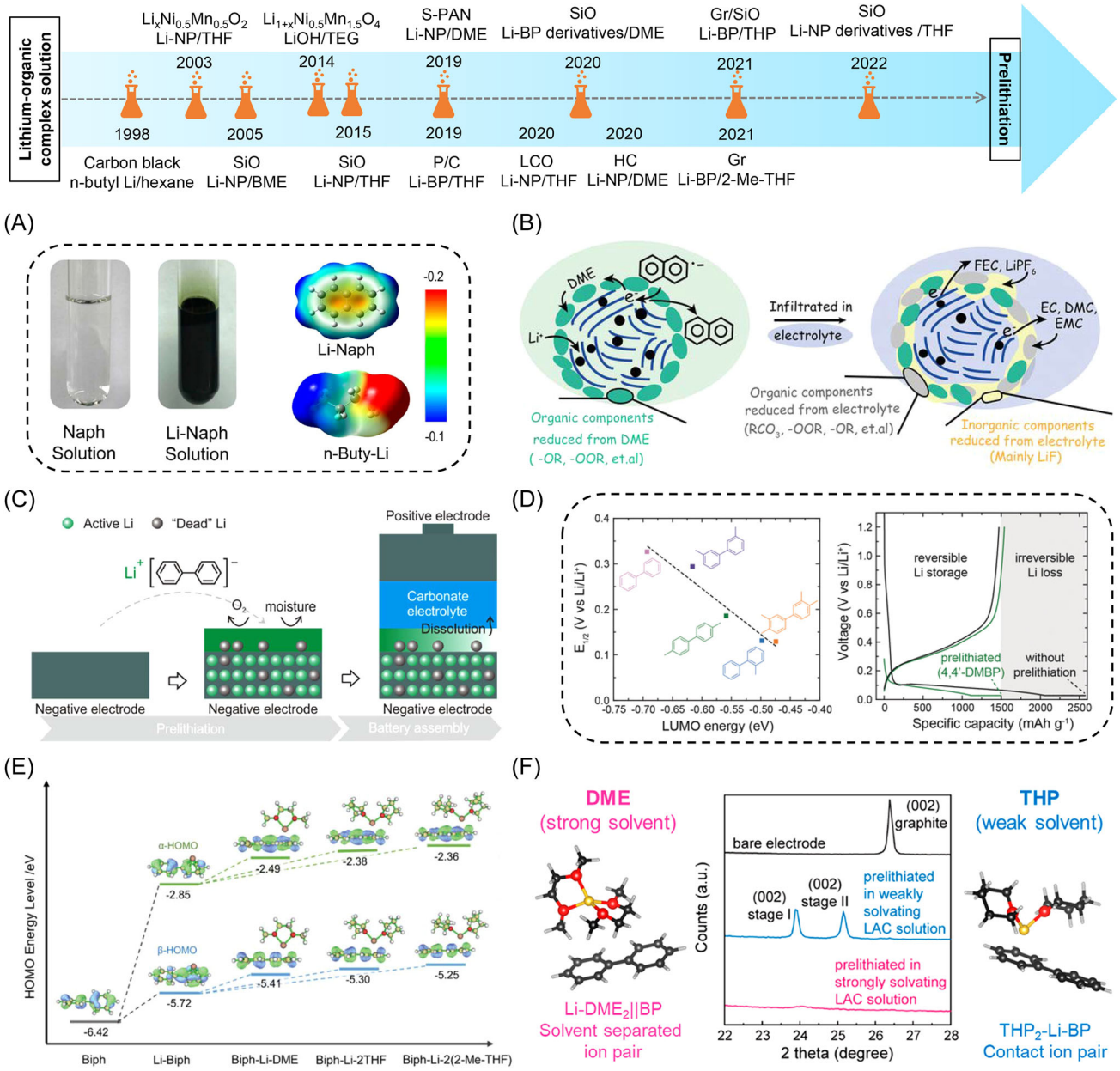

FIGURE 7 Representative studies on the lithium–organic complex solution prelithiation methods. (A) Photographs of NP and Li-NP in DME solvent (left); mapped electrostatic potential surfaces of NP anion and n-butyl anion (right). Reproduced with permission: Copyright 2019, American Chemical Society.[117] (B) Schematic illustration of the chemical prelithiation reaction for HC anodes in Li-NP/DME solution. Reproduced with permission: Copyright 2020, Wiley.[116] (C) Schematic illustration of the prelithiation process in Li-BP solution. Reproduced with permission: Copyright 2019, American Chemical Society.[118] (D) Correlation between the measured redox potential ($E_{1/2}$) of BP derivatives and the calculated LUMO energy (left); voltage profiles of the initial discharge–charge cycle of pristine and prelithiated SiO_x anodes (right). Reproduced with permission: Copyright 2020, Wiley.[119] (E) HOMO energy levels of the Li-BP–solvent complexes formed by Li–BP in three ethers of DME, THF, and 2-Me-THF, respectively. Reproduced with permission: Copyright 2021, Wiley.[120] (F) Schematic illustration of the Li^+ intercalation mechanism in different solvating solutions. Reproduced with permission: Copyright 2020, American Chemical Society.[121]

5 | PRELITHIATION DURING/AFTER BATTERY FABRICATION

Electrochemical prelithiation is usually achieved by preassembling the target electrode into a half-cell with lithium metal as the counter electrode, followed by various electrochemical steps. This strategy allows precise control over the prelithiation degree by adjusting experimental parameters. Numerous attempts have been made toward achieving high-performance batteries via electrochemical prelithiation.[90,127,128] For Ge–C anodes, galvanostatic cycling in lithium half-cells had been

applied to eliminate the ICL, which could enable capacity matching between Ge–C anodes and $LiCoO_2$ cathodes, further influencing the working voltage and cycle stability of the full-cells (Figure 8A).[129] Besides, Aurbach et al. prelithiated the HC anode to obtain the maximal capacity of full-cells and the specific capacity was enhanced from 92 to 162 mAh g^{-1} for the $LiNi_{0.5}Mn_{0.5}O_2$||HC full-cell. The same method is also suitable for presodiation in SIBs.[134] As shown in Figure 8B, Mullins et al. prelithiated a PbS electrode using a galvanostatic charge–discharge approach, converting the active material into Pb/Li_2S, which increased the ICE from 40% to >97%.[130] Recently, Dou et al. developed a thermal passivation strategy for the electrochemically prelithiated SiO_x@C anode (Figure 8C).[131] The treatment leaves a robust Li_2O passivating matrix on the anode surface, promoting its stability in air. However, these approaches not only require additional procedures including the disassembly of half-cells and the subsequent reassembly of full-cells but also increase the usage of electrolytes and separators.

Alternatively, a three-electrode pouch cell configuration with an inbuilt Li foil reservoir was proposed, which realizes in situ compensation of ICL of LIBs (Figure 8D).[132,135] The prelithiation process is driven by shorting the Li reservoir and the anode. The in situ replenishment of active lithium is more suitable for mass production without an additional battery disassembly process. Moreover, Chen et al. reported a Li-metal-free strategy to electrochemically prelithiate a Si anode in an electrolytic cell with a Li_2SO_4 aqueous solution (Figure 8E).[133] This is safer and potentially cheaper compared with that using Li metal, which is configured with a lithium super-ionic conductor (LISICON) separator.

For cathode, the electrochemical lithiation depth needs to be moderate; otherwise, it will cause structural degradation of materials. For instance, $LiCoO_2$ is converted into Li_2O, CoO, and Co metal after an overlithiation process under 1.2 V, leading to markedly deteriorated cycle performance.[136] Similarly, when the cubic $LiMn_2O_4$ is lithiated to the tetragonal $Li_2Mn_2O_4$, cycling stability will decrease due to the volume change. Madhavi et al. designed a cycling route to achieve the reversible Li^+ insertion of only tetrahedral region, in which overlithiated $Li_{1.26}Mn_2O_4$ compensated the ICL of the α-Fe_2O_3 anode in the full-cell.[137] Besides, the same method can also be applied to $LiNi_{0.5}Mn_{1.5}O_4$ because of its spinel structure with an approximately 4.7 V voltage platform.[30] In addition to the layered metal oxide cathode, Li et al. proposed an electrochemical strategy to prelithiate a phosphate cathode $Li_3V_2(PO_4)_3$ (L3VP).[138] Two Li per formula unit are doped into L3VP, forming $Li_5V_2(PO_4)_3$ (L5VP), which can be reversibly extracted. These extra Li^+ ions directly compensate for the lithium consumption of SEI and other side reactions on the HC anode.

6 | CONCLUSION AND OUTLOOK

During the past few decades, various prelithiation strategies have been developed to address the active lithium loss issue and improve the energy density of LIBs. It is worth pointing out that the appropriate prelithiation has a positive effect on the cycling stability of the LIBs, which is closely related to the degree of lithiation and the stability of preformed SEI. Additionally, it is able to compensate for the active lithium loss in the continuous cycling process. Table 1 summarizes the advantages and challenges of each prelithiation method for large-scale commercial applications based on various stages that they are implemented in. It should be noted that each prelithiation strategy has its practical application scenario based on the various industrial requirements. As shown in Figure 9, we have evaluated various prelithiation strategies in terms of accuracy, cost, convenience, uniformity, prelithiation capacity, and safety. In particular, we compared the uniformity of each prelithiation strategy. It is easier to achieve homogeneous lithiation based on the liquid-phase reaction compared with solid-phase reaction. In the following, critical analysis and meaningful perspectives are provided to facilitate the evolution of prelithiation strategies toward commercial practical applications:

(1) As a commercialized strategy for mass production, introduction of lithiation reagents into anode materials during their synthesis can effectively compensate for the ICL. However, issues such as large fluctuation in the degree of prelithiation and the relatively poor lithiation homogeneity should be addressed in the future. Besides, the lithium-rich phase directly synthesized by the solid-phase method has poor structural stability. Hence, optimization of lithium contents in the materials and reduction of the synthesis steps will be crucial to scale-up production.
(2) Loading of prelithiation additives into the electrode is another scalable strategy to provide additional lithium sources during slurry mixing. The future direction of the continuous research is to search for additives with high chemical stability and lithiation capacity, which could maintain electrode uniformity

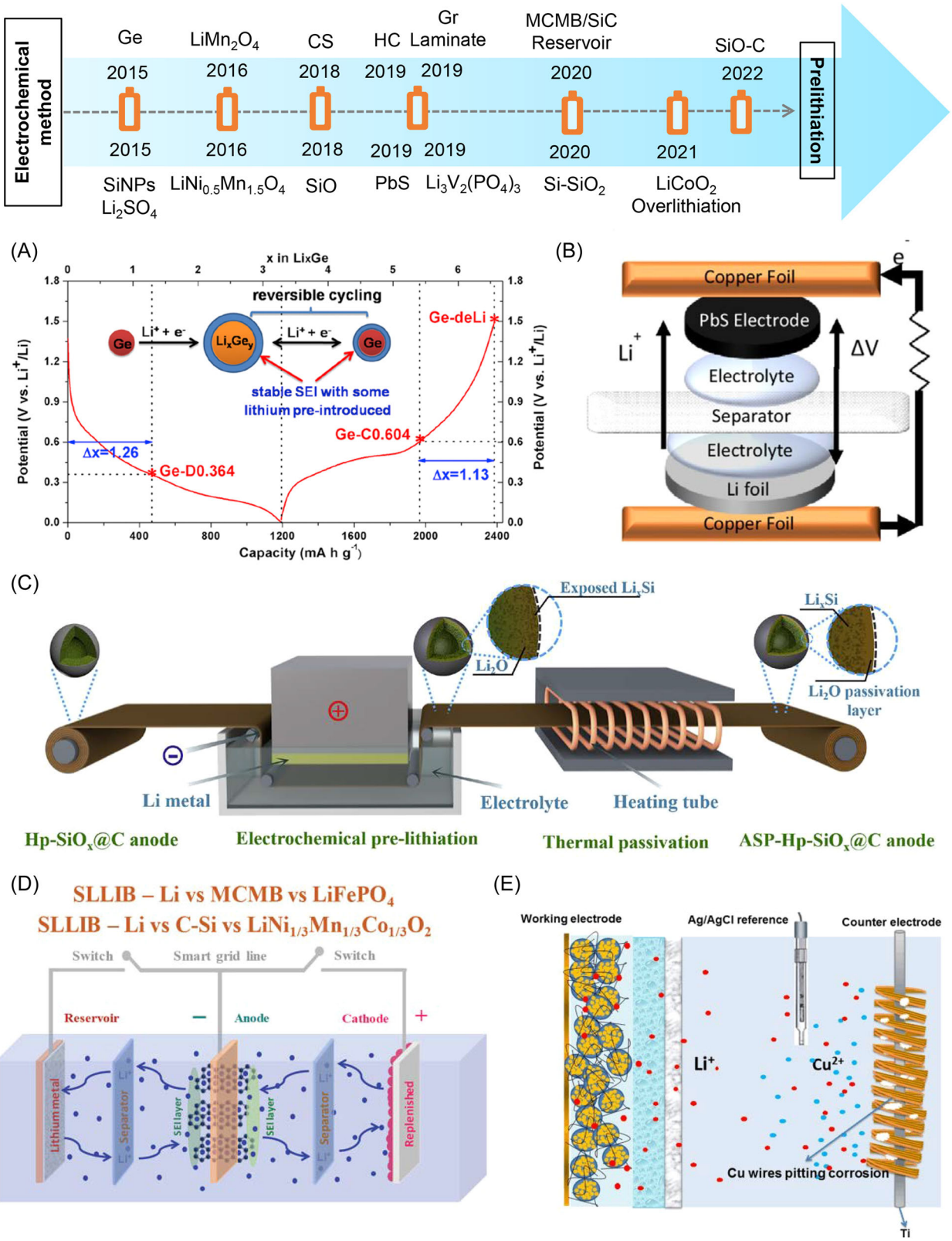

FIGURE 8 Representative studies on electrochemical prelithiation. (A) Schematic illustration of galvanostatic cycling for the Ge anode prelithiation. Reproduced with permission: Copyright 2015, Elsevier.[129] (B) Schematic illustration of the prelithiation setup for PbS electrodes. Reproduced with permission: Copyright 2019, Electrochemical Society.[130] (C) Schematic diagram of the large-scale roll-to-roll preparation of the ASP-Hp-SiO_x@C anode. Reproduced with permission: Copyright 2022, Elsevier.[131] (D) Schematic illustration of a synchronized lithium and lithium-ion battery. Reproduced with permission: Copyright 2020, Wiley.[132] (E) Principle of the prelithiation of the Si electrode using an electrolytic cell with a Cu pitting corrosion-type anodic half-cell in an aqueous electrolyte (0.5 M Li_2SO_4). Reproduced with permission: Copyright 2015, Wiley.[133]

TABLE 1 Summary of the advantages and challenges of various prelithiation strategies in large-scale practical applications

Prelithiation strategies		Advantages	Challenges
Prelithiation during material synthesis	Surface prelithiation	**1)** Simple operation **2)** Comparatively cheap raw material	**1)** Poor prelithiation effect and insufficient ICE improvement **2)** Uncontrolled degree of prelithiation **3)** Generation of the gas during slurry mixing
	Bulk prelithiation	**1)** Simple operation **2)** Rich and diverse lithium source	**1)** Strict processing condition **2)** Uncontrolled degree of prelithiation **3)** Generating the gas during slurry mixing
Prelithiation during slurry mixing	Anode prelithiation additive	**1)** Suitable prelithiation capacity and prelithiation effect **2)** Suitable low redox potential	**1)** Low additive utilization **2)** Poor industrial compatibility due to sensitivity to moisture and polar solvents
	Cathode prelithiation additive	**1)** Simple operation and easy large-scale production **2)** Suitable prelithiation capacity and prelithiation effect	**1)** Easy to gelate during the process **2)** Low additive utilization **3)** Promoting electrolyte decomposition **4)** Generating the extra inactive components and gas
Prelithiation during pretreatment of electrodes	Direct contact with Lithium metal	**1)** Simple operation **2)** High velocity of the prelithiation	**1)** Imprecise control for the degree of prelithiation **2)** Residual lithium dendrite **3)** Potential safety hazards
	Lithium–organic complex solution	**1)** Comparative control for the depth of lithiation **2)** Flexible adjustment for the formation of SEI	**1)** Unstable in ambient atmosphere **2)** Generating the organic waste solution
Prelithiation during/after battery fabrication	Electrochemical prelithiation	**1)** Accurate control of the depth of lithiation	**1)** Increasing the stage in battery fabrication

during the electrochemical process. Some principles used to seek prelithiation additives are as follows: (a) suitable reaction voltage; (b) high stability in ambient environment; (c) good compatibility with electrode components (i.e., active materials, electrolytes and binders); (d) environmental benignity and safety; and (e) low cost and facile synthesis.

(3) Direct contact with the lithium metal method and the lithium–organic complex solution method are the most common pretreatment methods for electrodes. Similarly, they introduce chemically active lithium into the electrode. Protecting lithium source against moisture, removing residue lithium, and cleaning prelithiated anode surface during the direct contact prelithiation process are the critical challenges in its large-scale application. In addition, it is necessary to manufacture thinner lithium foils (<5 μm) to accommodate relatively low specific capacity anode materials. As for solution method, the prelithiation degree for electrode could be adjusted by changing various complex solutes (e.g., NP and BP). At the same time, tuning complex solutions with weakly solvating solvents (e.g., 2-Me-THF and THP) can lower the redox potential and reduce the damage to the structure of active materials. Nonetheless, the lithium–organic complex solution is not stable in the moist air atmosphere, and prototype equipment for the continuous "soaking" process also needs to be designed.

(4) Electrochemical prelithiation could accurately control the amounts of lithium stored in the electrode through tuning the external current and voltage. By taking advantage of this strategy, we might be able to construct a desirable SEI/CEI film on the anode/cathode during the initial cycle by using electrolytes

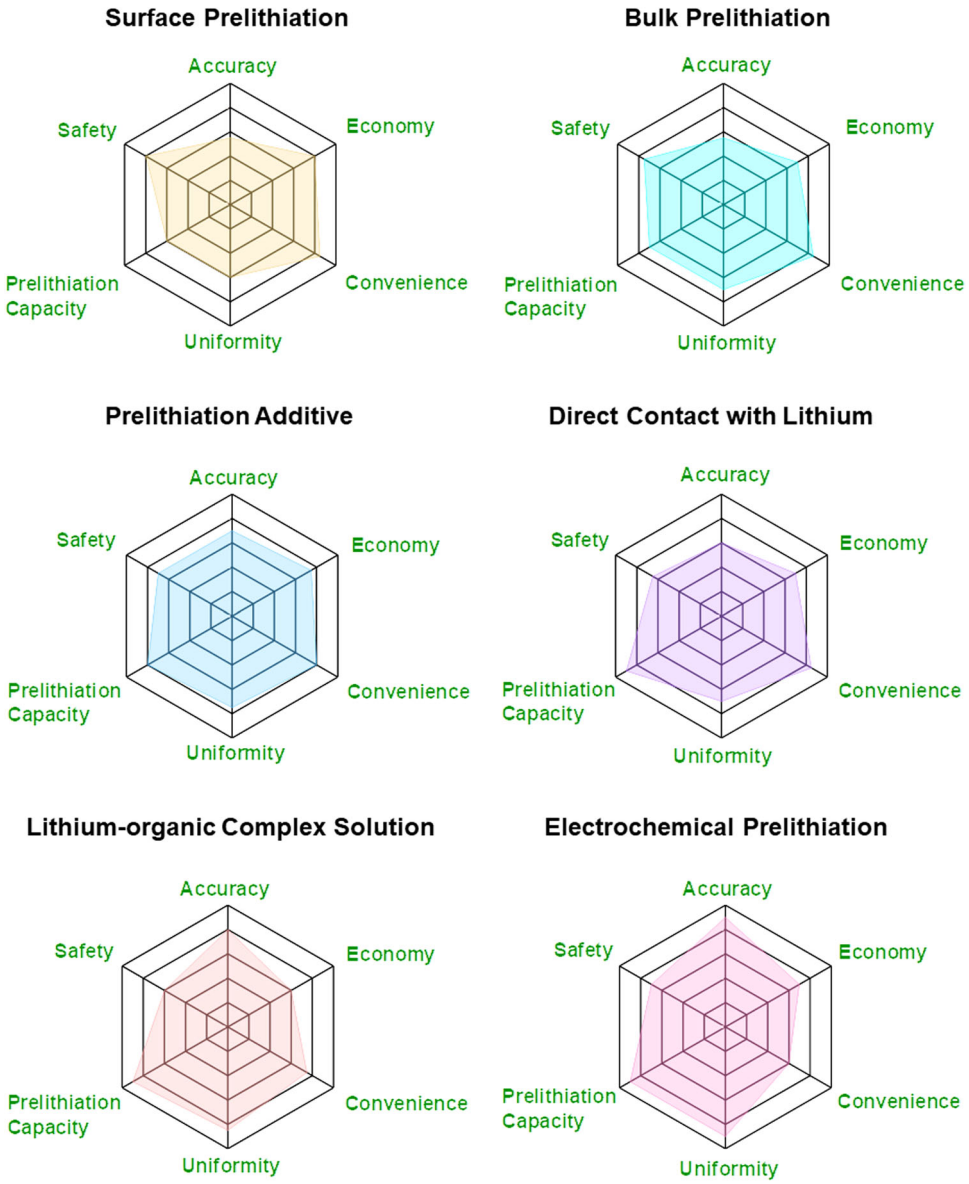

FIGURE 9 Radar charts for the evaluation of various prelithiation methods in terms of accuracy, cost, convenience, uniformity, prelithiation capacity, and safety (Note: The endpoint is better than the central point)

that might not be suitable for full-cells. However, complicated and expensive equipment design is required to achieve its large-scale industrialization. For instance, use of the three-electrode method requires a large Li-foil counter electrode, which will inevitably increase manufacturing costs and deteriorate high-temperature safety performance. It is also important to effectively protect the surface of electrochemical prelithiated electrodes from the ambient environment during the re-assembly.

As shown in Figure 10, from the perspective of thermodynamics, the equilibrium potential of reagents (V vs. Li/Li^+) directly affects the degree of lithiation. A suitable driving force is essential for uniform prelithiation. Sufficient reagent concentration is vital for prelithiation as well. Alternatively, conductivity, reaction interface, and temperature influence the in-depth distribution of lithiated regions kinetically. Therefore, on the one hand, favorable reaction thermodynamics and fast kinetics are required for efficient production; on the other hand, excessively intense reactions might cause current polarization at local areas, compromising the consistency and structural stability of the material.

Currently, the evolution mechanism and action principle of supplementary lithium sources in full-cells are unclear. Apart from prelithiation techniques, extra efforts also need to be dedicated to gain an understanding

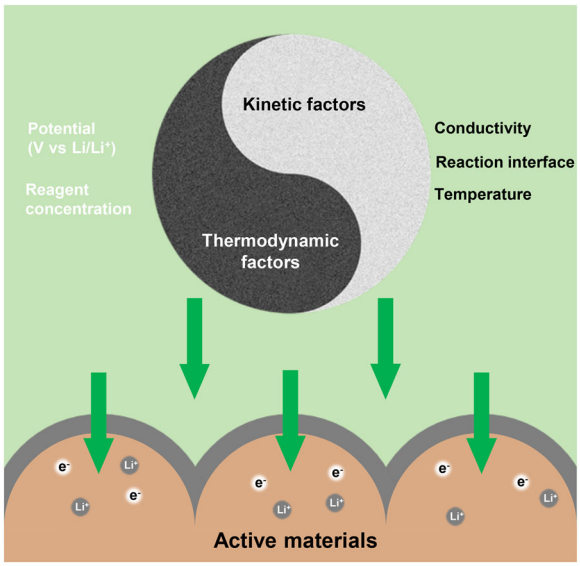

FIGURE 10 Schematic illustration of the factors affecting prelithiation

of various dynamic physicochemical processes of prelithiation (e.g., Li deposition, Li dissolution, and phase transformations) via in situ characterization techniques (e.g., in situ scanning electron microscope, in situ energy-dispersive spectroscopy, and in situ Raman spectroscopy). For each prelithiation strategy, it is necessary to analyze the in-depth distribution of lithiated regions in the bulk as well as the surface reconstruction of the active materials. Overall, similar strategies and mechanisms can be adopted for the optimization of SIBs and PIBs. For instance, suitable Na- or K-containing compounds can be screened for cathode additives based on the principles proposed in this work. With increasingly more attempts being made to improve the industrial practicability of prelithiation strategies, the commercialization of high-capacity batteries could be around the corner.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

ORCID

Feng Pan http://orcid.org/0000-0002-1362-4336
Luyi Yang http://orcid.org/0000-0002-5516-9829

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AUTHOR BIOGRAPHIES

Shiming Chen received his bachelor's degree from the Institute for Advanced Study, Nanchang University (China), in 2020. He is currently a PhD candidate under the supervision of Prof. Feng Pan in the School of Advanced Materials, Peking University Shenzhen Graduate School, China. His research focuses on the anode materials of lithium-ion batteries and quantum chemical calculation.

Zhen Wang is currently a master's degree candidate under the supervision of Prof. Feng Pan in School of Advanced Materials, Peking University Shenzhen Graduate School, China. He obtained his bachelor's degree from the School of Materials Science and Chemical Engineering, Ningbo University (China), in 2021. His research focuses on the presodiation of sodium-ion batteries.

Meng Zhang received her PhD degree from Xiamen University in 2015 under the supervision of Prof. Bing-Wei Mao and Zhong-Qun Tian. Dr. Zhang is currently a manager at the BTR New Energy Technology Research Institute. Her research interests mainly focus on the reaction mechanisms and failure analysis in Li-ion batteries and new energy materials.

Xiaoze Shi received her bachelor and master degrees degrees from Soochow University (China) in 2011 and 2014. She obtained her PhD degree from West Pomeranian University of Technology in Szczecin (Poland) in 2019. In 2021, Dr. Shi joined Shenzhen BAK Power Battery CO., Ltd in China as a deputy senior engineer. Her research interest is the development of silicon-based anode materials and prelithiation technologies for High performance lithium ion batteries.

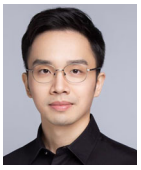
Lu Wang is currently a master's degree candidate in School of Advanced Materials, Peking University Shenzhen Graduate School, China, under the supervision of Prof. Feng Pan. He graduated with a bachelor's degree from College of Materials Science and Chemical Engineering, Harbin

Engineering University (China) in 2020. His research interests include Si-based anodes and binders of lithium-ion batteries.

Weifeng An received his master degree from Beijing Institute of Technology in 2009. And now He is in charge of technology innovation division of Shenzhen BAK Power Battery Co., Ltd. His research focuses on high-nickel cathode material, silicon anode material, electrolyte, separator and failures analysis of lithium ion batteries.

Zikun Li received his PhD degree from Hong Kong Baptist University in 2011. Dr. Li is currently the president of the BTR New Energy Technology Research Institute. His research interests mainly focus on the new material development and industrialization for batteries, and new energy technology research.

Feng Pan is chair-professor, VP Peking University Shenzhen Graduate School, Founding Dean of School of Advanced Materials, and director of the National Center of Electric Vehicle Power Battery and Materials for International Research. He received his bachelor's degree from the Department of Chemistry, Peking University, in 1985 and PhD degree from the Department of P&A Chemistry, University of Strathclyde (UK). Prof. Pan has been engaged in fundamental research of structure chemistry, exploring "Material Gene" for Li-ion batteries, and developing novel energy conversion-storage materials & devices.



Luyi Yang received his bachelor's degree from the Department of Chemistry at Xiamen University (China) in 2010 and earned his PhD degree from the School of Chemistry at Southampton University (UK) in 2015 under the supervision of Prof. John Owen. He is currently an associate research professor at the School of Advanced Materials, Peking University, Shenzhen Graduate School. His research interests mainly focus on the investigation of key materials in lithium batteries.

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