CARBON ENERGY WILEY

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

Shiming Chen¹ | Zhen Wang¹ | Meng Zhang² | Xiaoze Shi³ | Lu Wang¹ | Weifeng An³ | Zikun Li² | Feng Pan¹ \square | Luyi Yang¹ \square

¹School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen, China
 ²BTR New Material Group Co., Ltd., Shenzhen, China
 ³R&D Institute, Shenzhen BAK Power Battery Co., Ltd., Shenzhen, China

Revised: 24 September 2022

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

Funding information

Soft Science Research Project of Guangdong Province, Grant/Award Number: 2017B030301013; Shenzhen Science and Technology Research Grant, Grant/Award Number: JCYJ20200109140416788

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.

K E Y W O R D S

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.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2023 The Authors. Carbon Energy published by Wenzhou University and John Wiley & Sons Australia, Ltd.

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., LiCoO₂ and LiFePO₄) 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



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

work has reference value to the presodiation/prepotassiation toward high-performance sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs).

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 LiBH₄ as the prelithiation reagent to construct an artificial SEI film (Li₂SiO₃) 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 SnO₂ 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 CARBON ENERGY-WILEY

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 LiCoO₂ cathode material in a Li-naphthalene (NP)/tetrahydrofuran (THF) solution to form a Li₂O/Co nanoshell on the surface of LiCoO₂ particles (Figure 2D).¹² The Li₂O/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 Li₂O/Co shell can be regulated by adjusting the ratio of Li–NP to LiCoO₂, 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_x Si 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/Li₂SiO₃@C composites via a facile method using SiO, pitch powder, and Li₂CO₃–PVA, solution followed by annealing treatment. Reproduced with permission: Copyright 2019, Royal Society of Chemistry.¹⁰ (C) Schematic of LiF@SnO₂@C nanosheets using the ball-milling method. Reproduced with permission: Copyright 2021, Elsevier.¹¹ (D) Schematic illustration of the preparation of a Li₂O/Co nanoshell-coated LiCoO₂ by a chemical reaction between Li-NP and LiCoO₂. 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/SiO₂ and lithium powders under an argon atmosphere, generating irreversible phases (Li₂SiO₃, Li₄SiO₄, 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 TiO₂-encapsulated silicon nanoparticles were chosen and mixed with molten lithium metal to obtain a Li_xSi-Li₂O/Ti_vO_z composite anode (Figure 3A).¹⁶ The prelithiated TiO_2 protective layer (Li_2O/Ti_vO_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 $SiO_r/Mg_2SiO_4/SiO_r$ 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 Li₂SiO₃ 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_r/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}O₂ (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 ZnMoO₄, 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 LiMn₂O₄ cathode can store extra irreversible Li⁺ with the help of the Mn⁴⁺/Mn³⁺ 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 LiMn₂O₄ cathode is a feasible method to compensate for the anodic ICL in a full battery. As early as 1991, Tarascon et al. prepared Li₂Mn₂O₄ by heating a vacuumencapsulated mixture of LiMn₂O₄ 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), $LiNi_{0.5}M$ $n_{1,5}O_4$ (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}O₄ (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 fullcells.^{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-Li₂O/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}O₂ 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}O₄ via stirring Li_{1.0}Ni_{0.5}Mn_{1.5}O₄ 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 $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O_2^{-3}$ were synthesized using the spray-drying method, overlithiated Li_{1+x}Ni_{0.8}Co_{0.2}O₂³⁶ was synthesized using the combustion/annealing method, and lithium-rich $xLi_2MnO_3 \cdot (1-x)Li[Mn_vNi_zCo_{1-v-z}]O_2^{37}$ 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 Sibased 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-Li₂O core-shell nanoparticles synthesized from nanosilicon 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-Li₂O core-shell nanoparticles were exposed to moisture-laden air, their capacity decreased markedly. To enhance the resistance of LixSi to moisture, they treated Li_xSi nanoparticles with a nonpolar 1fluorodecane/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/Li₂O composites obtained by replacing nanosilicon with SiO or SiO₂ showed superior ambient environment compatibility $(1240 \text{ mAh g}^{-1} \text{ capacity after } 6 \text{ h of}$ exposure to 40% RH).⁴⁰ In the Li_xSi/Li₂O composite structure, the Li_xSi nanodomains are uniformly distributed in the crystalline Li₂O matrix, resulting in a huge contact area between Li_xSi and Li₂O (Figure 4B). According to density functional theory (DFT) theoretical calculations, there is a strong interaction between the oxygen atom in Li₂O and the lithium atom in Li₂Si, which effectively stabilizes lithium atoms in Li, Si. Therefore, compared with the core-shell Li_xSi-Li₂O composite, the Li_xSi/Li₂O 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_yZ alloys, the Li_yGe 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 selfassembled 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 Gr⁴⁹ 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/Li₂O 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, Li₂CuO₂⁵¹ and Li₂NiO₂⁵²⁻⁵⁴ were developed as prelithiation additives for LiMn₂O₄ and LiCoO₂ cathodes, respectively. Although Li₂NiO₂ has a higher capacity than Li₂CuO₂, Li₂CuO₂ is completely stable in air, while Li₂NiO₂ is sensitive to moisture, which is unfavorable for industrial production. To make up for this shortcoming of Li₂NiO₂, Al₂O₃-coated Li₂NiO₂ was successfully prepared through the reaction of Al iso-propoxide with Li₂NiO₂.⁵⁵ The Al₂O₃ protective layer

significantly improved the ambient stability of Li₂NiO₂. 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 delithiation potential (3.5-4.0 V), Li₅FeO₄ (LFO) showed excellent prelithiation ability as a cathode additive.^{56–60} Lu et al. added 7 wt% LFO to the LiCoO₂ cathode to increase the reversible capacity of the LiCoO2||HC fullcell 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 Fe₃O₄/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 $(1675 \text{ mAh g}^{-1})$,⁶⁵ Li₂O₂ $(1168 \text{ mAh g}^{-1})$,⁶⁶ and so forth. In 2010, Armand et al. first proposed LiN₃ as a positive sacrificial salt to compensate for the ICL of an anode.⁶⁷ However, the toxicity of LiN₃ limits its largescale application and research. As an alternative to LiN₃, Li₃N is safer and has much higher capacity; thus, it is more suitable as a cathode prelithiation additive. Nevertheless, Li₃N only stably exists in dry air⁶⁴ and it is not compatible with NMP.⁶⁸ To tackle these issues, Cui et al. constructed a dense passivation layer composed of Li₂O and Li₂CO₃ on the surface of Li₃N by annealing,⁶⁸ and similarly, Chen et al. directly aged Li₃N in dry air to obtain a Li₂CO₃ coating.⁶⁹ Compared with Li₃N, Li₂O 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, Li₂O also readily reacts with moisture to form LiOH, resulting in poor ambient tolerance. To circumvent this shortcoming, Johnson et al. introduced a Co₃O₄ coating onto the Li₂O surface by ball milling.⁷⁰ As a promising additive, Li₂O₂ has low conductivity, leading to a decomposition capacity of 171.1 mAh g^{-1} at 4.6 Vversus 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 Li₂O₂ activation and promote the decomposition of Li₂O₂. As with Li₂O₂, 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, Li₂S, Li₂O, 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 Li₂S/ Co (670 mAh g^{-1}) ,⁷⁸ Li₂S/Fe (480 mAh g^{-1}) ,⁷⁸ Li₂O/Co (609 mAh g^{-1}) ,⁷⁴ Li₂O/Fe (612 mAh g^{-1}) ,⁷⁴ Li₂O/Ni (495 mAh g^{-1}) ⁷⁴ and so on. Adding these prelithiation species to the cathode can effectively improve the firstcycle charge capacity and compensate for the ICL of the anode. For instance, the charge capacity of LiFePO₄ with a 4.8% Li₂S/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/Li₂O 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 CoF₃ 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/Li₂O nanocomposites in ambient air. Reproduced with permission: Copyright 2020, American Chemical Society.⁷⁵

more homogeneous composite, Qiu et al. used Li₂CO₃/C composites and $FeC_2O_4 \cdot 2H_2O$ as raw materials to prepare Fe/Li₂O 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.

PRELITHIATION DURING 4 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-Fe₃O₄,⁸² 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 $50 \,\mu\text{m}$, 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 Li₂CO₃ (3 wt%) protection layer (~350 nm). Hence, a pressure activation process is normally required to crack the Li₂CO₃ 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 H₂O). 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}O₂||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-cobutadiene) 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/Li₂O protective shell.¹⁰⁸ The superior electrochemical performance of ASLSs is attributed to the small and uniform particle size $(0.5-3 \,\mu\text{m})$ 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 indepth 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.

12 of 23

WILEY-CARBON ENERGY-

Also, prelithiation can be achieved by coating the electrode surface with Li-rich compounds. Fu et al. deposited Li on the LiFePO₄ cathode surface by thermal deposition and synthesized an alpha-Li₃N film under a nitrogen atmosphere.¹⁰⁹ The discharge capacity of the LiFePO₄||Gr full-cell increased by 30.7% with 1% Li₃N coating. Moreover, the slurry containing Li₂S 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, ROCO₂Li) 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 prelithation.^{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 anode¹²⁴ and a SnO₂/C nanocomposite anode¹²⁵ 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-workers¹²¹ 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

PRELITHIATION DURING/ 5 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 LiCoO₂ 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/Li₂S, 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 Li₂O 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, LiCoO₂ is converted into Li₂O, 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}Mn₂O₄ compensated the ICL of the α -Fe₂O₃ anode in the full-cell.¹³⁷ Besides, the same method can also be applied to LiNi0.5Mn1.5O4 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 Li₂SO₄). Reproduced with permission: Copyright 2015, Wiley.¹³³

of

Prelithiation strategies		Advantages	Challenges
Prelithiation during material synthesis	Surface prelithiation	 Simple operation Comparatively cheap raw material 	 Poor prelithiation effect and insufficient ICE improvement Uncontrolled degree of prelithiation Generation of the gas during slurry mixing
	Bulk prelithiation	 Simple operation Rich and diverse lithium source 	 Strict processing condition Uncontrolled degree of prelithiation Generating the gas during slurry mixing
Prelithiation during slurry mixing	Anode prelithiation additive	1) Suitable prelithiation capacity and prelithiation effect	 Low additive utilization Poor industrial compatibility due to

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

		2)	Suitable low redox potential		sensitivity to moisture and polar solvents
	Cathode prelithiation additive	1) 2)	Simple operation and easy large-scale production Suitable prelithiation capacity and prelithiation effect	1) 2) 3) 4)	Easy to gelate during the process Low additive utilization Promoting electrolyte decomposition Generating the extra inactive components and gas
Prelithiation during pretreatment of electrodes	Direct contact with Lithium metal	1) 2)	Simple operation High velocity of the prelithiation	1) 2) 3)	Imprecise control for the degree prelithiation Residual lithium dendrite Potential safety hazards
	Lithium–organic complex solution	1) 2)	Comparative control for the depth of lithiation Flexible adjustment for the formation of SEI	1) 2)	Unstable in ambient atmosphere 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 ($<5 \mu m$) 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 energydispersive 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.

ACKNOWLEDGMENTS

The authors acknowledge financial support from The Shenzhen Science and Technology Research Grant (No. JCYJ20200109140416788) and the Soft Science Research Project of Guangdong Province (No. 2017B030301013).

CONFLICT OF INTEREST

The authors declare that there are no conflict of interests.

ORCID

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

REFERENCES

- Min X, Xu G, Xie B, Guan P, Sun M, Cui G. Challenges of prelithiation strategies for next generation high energy lithium-ion batteries. *Energy Storage Mater.* 2022;47:297-318.
- Shellikeri A, Watson V, Adams D, et al. Investigation of pre-lithiation in graphite and hard-carbon anodes using different lithium source structures. *J Electrochem Soc.* 2017; 164(14):A3914-A3924.
- 3. Xin C, Gao J, Luo R, Zhou W. Frontispiece: prelithiation reagents and strategies on high energy Lithium-Ion batteries. *Chemistry*. 2022;28(23):e202104282.
- Park CM, Kim JH, Kim H, Sohn HJ. Li-alloy based anode materials for Li secondary batteries. *Chem Soc Rev.* 2010; 39(8):3115-3141.
- Obrovac MN, Chevrier VL. Alloy negative electrodes for Liion batteries. *Chem Rev.* 2014;114(23):11444-11502.
- Chen S, Song Z, Wang L, et al. Establishing a resilient conductive binding network for Si-based anodes via molecular engineering. *Acc Chem Res.* 2022;55(15):2088-2102.
- Wang F, Wang B, Li J, et al. Prelithiation: a crucial strategy for boosting the practical application of next-generation lithium ion battery. ACS Nano. 2021;15(2):2197-2218.
- Chen S, Wang Z, Wang L, et al. Constructing a robust solid-electrolyte interphase layer via chemical prelithiation for high-performance SiO_x anode. *Adv Energy Sustain Res.* 2022;3(10):2200083.
- 9. Alaboina PK, Cho JS, Uddin MJ, Cho SJ. Mechanically prelithiated silicon nano alloy as highly engineered anode material. *Electrochim Acta*. 2017;258:623-630.
- Xie L, Liu H, Lin S, et al. Modified SiO hierarchical structure materials with improved initial coulombic efficiency for advanced lithium-ion battery anodes. *RSC Adv.* 2019;9(20): 11369-11376.
- 11. Wu K, Feng Y, Ke J, et al. Stabilizing the nanostructure of pre-lithiated LiF nanoparticles modified SnO₂@graphite nanosheets as a high performance anode material for lithium ions batteries. *Ceram Int.* 2021;47(16):22776-22785.
- 12. Liu X, Tan Y, Wang W, et al. Conformal prelithiation nanoshell on $LiCoO_2$ enabling high-energy lithium-ion batteries. *Nano Lett.* 2020;20(6):4558-4565.
- Zhu Y, Hu W, Zhou J, et al. Prelithiated surface oxide layer enabled high-performance Si anode for lithium storage. ACS Appl Mater Interfaces. 2019;11(20):18305-18312.
- Domi Y, Usui H, Iwanari D, Sakaguchi H. Effect of mechanical pre-lithiation on electrochemical performance of silicon negative electrode for lithium-ion batteries. *J Electrochem Soc.* 2017;164(7):A1651-A1654.
- Yom JH, Seong IW, Cho SM, Yoon WY. Optimization of heat treatment conditions for fabricating pre-lithiated silicon monoxide as an anode material for lithium-ion batteries. *J Electrochem Soc.* 2018;165(3):A603-A608.
- Wang C, Han Y, Li S, Chen T, Yu J, Lu Z. Thermal lithiated-TiO₂: a robust and electron-conducting protection layer for Li-Si alloy anode. ACS Appl Mater Interfaces. 2018;10(15):12750-12758.
- Chung DJ, Youn D, Kim S, et al. Dehydrogenation-driven Li metal-free prelithiation for high initial efficiency SiO-based lithium storage materials. *Nano Energy*. 2021;89:106378.

- Yan MY, Li G, Zhang J, et al. Enabling SiO_x/C anode with high initial coulombic efficiency through a chemical prelithiation strategy for high-energy-density lithium-ion batteries. ACS Appl Mater Interfaces. 2020;12(24):27202-27209.
- Jang J, Ki H, Kang Y, et al. Chemically prelithiated graphene for anodes of Li-ion batteries. *Energy Fuels*. 2020;34(10): 13048-13055.
- 20. Liu X, Liu T, Wang R, et al. Prelithiated Li-enriched gradient interphase toward practical high-energy NMC-Silicon full cell. *ACS Energy Lett.* 2021;6(2):320-328.
- Moorhead-Rosenberg Z, Allcorn E, Manthiram A. In situ mitigation of first-cycle anode irreversibility in a new spinel/ FeSb lithium-ion cell enabled via a microwave-assisted chemical lithiation process. *Chem Mater.* 2014;26(20):5905-5913.
- Betz J, Nowak L, Winter M, Placke T, Schmuch R. An approach for pre-lithiation of Li_{1+x}Ni_{0.5}Mn_{1.5}O₄ cathodes mitigating active lithium loss. *J Electrochem Soc.* 2019; 166(15):A3531-A3538.
- Wang H, Man H, Yang J, et al. Self-adapting electrochemical grinding strategy for stable silicon anode. *Adv Funct Mater*. 2022;32(6):2109887.
- Raza A, Jung JY, Lee CH, et al. Swelling-controlled doublelayered SiO_x/Mg₂SiO₄/SiO_x composite with enhanced initial coulombic efficiency for lithium-ion battery. *ACS Appl Mater Interfaces*. 2021;13(6):7161-7170.
- Wan Y, Wang L, Chen Y, et al. A high-performance tin dioxide@carbon anode with a super high initial Coulombic efficiency via a primary cell prelithiation process. J Alloys Compd. 2018;740:830-835.
- Masood KB, Parte G, Jain N, et al. Electrochemical performance of pre-lithiated ZnMoO₄ and r-Go@ZnMoO₄ composite anode for lithium-ion battery application. *J Taiwan Inst Chem Eng.* 2020;112:60-66.
- Kosilov Vv, Potapenko Av, Kirillov SA. Effect of overdischarge (overlithiation) on electrochemical properties of LiMn₂O₄ samples of different origin. J Solid State Electrochem. 2017;21(11):3269-3279.
- 28. Tarascon JM, Guyomard D. Li metal-free rechargeable batteries based on Li_{1+x} Mn₂O₄ cathodes ($0 \le x \le 1$) and carbon anodes. *J Electrochem Soc.* 1991;138:2864-2868.
- Peramunage D, Abraham KM. Preparation and electrochemical characterization of overlithiated spinel LiMn₂O₄. *J Electrochem Soc.* 1998;145(4):1131-1136.
- 30. Aravindan V, Arun N, Shubha N, Sundaramurthy J, Madhavi S. Overlithiated $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in all one dimensional architecture with conversion type α -Fe₂O₃: a new approach to eliminate irreversible capacity loss. *Electrochim Acta*. 2016;215:647-651.
- Gabrielli G, Marinaro M, Mancini M, Axmann P, Wohlfahrt-Mehrens M. A new approach for compensating the irreversible capacity loss of high-energy Si/ClLiNi_{0.5}Mn_{1.5}O₄ lithium-ion batteries. *J Power Sources*. 2017;351:35-44.
- Mancini M, Axmann P, Gabrielli G, Kinyanjui M, Kaiser U, Wohlfahrt-Mehrens M. A high-voltage and high-capacity Li_{1+x}Ni_{0.5}Mn_{1.5}O₄ cathode material: from synthesis to full lithium-ion cells. *ChemSusChem*. 2016;9(14):1843-1849.
- 33. Dose WM, Blauwkamp J, Piernas-Muñoz MJ, et al. Liquid ammonia chemical lithiation: an approach for high-energy

and high-voltage Si-graphite|Li_{1+x}Ni_{0.5}Mn_{1.5}O₄ Li-ion batteries. *ACS Appl Energy Mater*. 2019;2(7):5019-5028.

CARBON ENERGY-WILEY

- 34. Kim JM, Kumagai N, Cho TH. Synthesis, structure, and electrochemical characteristics of overlithiated $\text{Li}_{1+x}(\text{Ni}_{z-}\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ ($z = 0.1 \sim 0.4$ and $x = 0.0 \sim 0.1$) positive electrodes prepared by spray-drying method. *J Electrochem Soc.* 2008;155(1):A82-A89.
- Kim JM, Kumagai N, Chung HT. Improved electrochemical properties and structural stability of overlithiated Li_{1+x} (Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O₂ prepared by spray-drying method. *Electrochem Solid-State Lett.* 2006;9(11):A494-A498.
- Rusdi R, Kamarulzaman N, Elong K, Rusdi H, Abd-Rahman A. Electrochemical performance of overlithiated Li_{1+x}Ni_{0.8} Co_{0.2}O₂: structural and oxidation state studies. *Front Mater Sci.* 2015;9(2):199-205.
- Jo YN, Prasanna K, Park SJ, Lee CW. Characterization of Li-rich xLi₂MnO₃*(1-x)Li[Mn_yNi_zCo_{1-y-z}]O₂ as cathode active materials for Li-ion batteries. *Electrochim Acta*. 2013;108:32-38.
- Zhao J, Lu Z, Wang H, et al. Artificial solid electrolyte interphase-protected Li_xSi nanoparticles: an efficient and stable prelithiation reagent for lithium-ion batteries. *J Am Chem Soc.* 2015;137(26):8372-8375.
- Zhao J, Lu Z, Liu N, Lee HW, McDowell MT, Cui Y. Dry-airstable lithium silicide-lithium oxide core-shell nanoparticles as high-capacity prelithiation reagents. *Nat Commun.* 2014;5: 5088.
- 40. Zhao J, Lee HW, Sun J, et al. Metallurgically lithiated SiO_x anode with high capacity and ambient air compatibility. *Proc Natl Acad Sci USA*. 2016;113(27):7408-7413.
- Zhao J, Sun J, Pei A, et al. A general prelithiation approach for group IV elements and corresponding oxides. *Energy Storage Mater.* 2018;10:275-281.
- Zhao X, Yi R, Zheng L, et al. Practical prelithiation of 4.5V LiCoO₂||graphite batteries by a passivated lithium-carbon composite. *Small.* 2022;18(9):2106394.
- Takeda Y, Yang J. New composite anode systems combined with Li_{2.6}Co_{0.4}N. J Power Sources. 2001;97-98:244-246.
- Shodai T. Study of Li_{3-x}M_xN (M: Co, Ni or Cu) system for use as anode material in lithium rechargeable cells. *Solid State Ionics*. 1996;86-88:785-789.
- Yang J, Takeda Y, Imanishi N, Xie JY, Yamamoto O. Morphology modification and irreversibility compensation for SnO anodes. *J Power Sources*. 2001;97-98:216-218.
- 46. Yang J, Takeda Y, Imanishi N, Yamamoto O. Novel composite anodes based on nano-oxides and $Li_{2.6}Co_{0.4}N$ for lithium ion batteries. *Electrochim Acta*. 2001;46(17):2659-2664.
- Liu Y, Hanai K, Horikawa K, Imanishi N, Hirano A, Takeda Y. Electrochemical characterization of a novel Sigraphite-Li_{2.6}Co_{0.4}N composite as anode material for lithium secondary batteries. *Mater Chem Phys.* 2005;89(1):80-84.
- Sun H, He X, Li J, Ren J, Jiang C, Wan C. Hard carbon/ Li_{2.6}Co_{0.4}N composite anode materials for Li-ion batteries. *Solid State Ion*. 2006;177(15-16):1331-1334.
- Liu D, Du F, Pan W, Chen G, Wang C, Wei Y. Electrochemical characterizations of Li_{2.6}Co_{0.4}N/graphite anodes for lithium ion batteries. *Mater Lett.* 2009;63(3-4): 504-506.

CHEN ET AL.

26379368, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/cey2.323 by University Town Of Shenzhen, Wiley Online Library on [15/05/2023]. See the Terms

and Conditions (https://onlinelibrary.wiley.com/term

and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

WILEY-CARBON ENERGY-

- West K, Vitins G, Koksbang R. Synthesis and host properties of tetragonal Li₂Mn₂O₄ and Li₂Co_{0.4}Mn_{1.6}O₄. *Electrochim Acta*. 2000;45(19):3141-3149.
- Vitins G, Raekelboom EA, Weller MT, Owen JR. Li₂CuO₂ as an additive for capacity enhancement of lithium ion cells. *J Power Sources*. 2003;119-121:938-942.
- Lee H, Chang SK, Goh EY, et al. Li₂NiO₂ as a novel cathode additive for overdischarge protection of Li-ion batteries. *Chem Mater.* 2008;20(1):5-7.
- Park H, Yoon T, Kim YU, Ryu JH, Oh SM. Li₂NiO₂ as a sacrificing positive additive for lithium-ion batteries. *Electrochim Acta*. 2013;108:591-595.
- Kim J, Kang H, Hwang K, Yoon S. Thermal decomposition study on Li₂O₂ for Li₂NiO₂ synthesis as a sacrificing positive additive of lithium-ion batteries. *Molecules*. 2019;24(24):4624.
- Kim MG, Cho J. Air stable Al₂O₃-coated Li₂NiO₂ cathode additive as a surplus current consumer in a Li-ion cell. *J Mater Chem.* 2008;18(48):5880-5887.
- Hirano A, Matsumura T, Ueda M, Imanishi N, Takeda Y, Tabuchi M. Electrochemical properties and mössbauer effect of anti-fluorite type compound, Li₅FeO₄. *Solid State Ionics*. 2005;176(37-38):2777-2782.
- 57. Johnson CS, Kang SH, Vaughey JT, Pol Sv, Balasubramanian M, Thackeray MM. Li_2O removal from Li_5FeO_4 : a cathode precursor for lithium-ion batteries. *Chem Mater.* 2010;22(3):1263-1270.
- Zhang L, Dose WM, Vu AD, Johnson CS, Lu W. Mitigating the initial capacity loss and improving the cycling stability of silicon monoxide using Li₅FeO₄. *J Power Sources*. 2018;400: 549-555.
- Dose WM, Villa C, Hu X, et al. Beneficial effect of Li₅FeO₄ lithium source for Li-ion batteries with a layered NMC cathode and Si anode. *J Electrochem Soc.* 2020;167(16):160543.
- Lee SW, Kim HK, Kim MS, Roh KC, Kim KB. A study of the effects of synthesis conditions on Li₅FeO₄/carbon nanotube composites. *Sci Rep.* 2017;7:46530.
- Su X, Lin C, Wang X, et al. A new strategy to mitigate the initial capacity loss of lithium ion batteries. *J Power Sources*. 2016;324:150-157.
- Chen Z, Zhang Z, Li J. Polyhedral perspectives on the capacity limit of cathode compounds for lithium-ion batteries: a case study for Li₆CoO₄. *Phys Chem Chem Phys.* 2018;20(31):20363-20370.
- Noh M, Cho J. Role of Li₆CoO₄ cathode additive in Li-ion cells containing low coulombic efficiency anode material. *J Electrochem Soc.* 2012;159(8):A1329-A1334.
- Park K, Yu BC, Goodenough JB. Li₃N as a cathode additive for high-energy-density lithium-ion batteries. *Adv Energy Mater.* 2016;6(10):1502534.
- Abouimrane A, Cui Y, Chen Z, et al. Enabling high energy density Li-ion batteries through Li₂O activation. *Nano Energy*. 2016;27:196-201.
- Bie Y, Yang J, Wang J, Zhou J, Nuli Y. Li₂O₂ as a cathode additive for the initial anode irreversibility compensation in lithium-ion batteries. *Chem Commun*. 2017;53(59):8324-8327.
- Shanmukaraj D, Grugeon S, Laruelle S, Douglade G, Tarascon JM, Armand M. Sacrificial salts: compensating the initial charge irreversibility in lithium batteries. *Electrochem Commun.* 2010;12(10):1344-1347.

- Sun Y, Li Y, Sun J, Li Y, Pei A, Cui Y. Stabilized Li₃N for efficient battery cathode prelithiation. *Energy Storage Mater*. 2017;6:119-124.
- Bian X, Pang Q, Wei Y, Zhang D, Gao Y, Chen G. Dual roles of Li₃N as an electrode additive for Li-excess layered cathode materials: a Li-ion sacrificial salt and electrode-stabilizing agent. *Chemistry*. 2018;24(52):13815-13820.
- 70. Ha Y, Schulze MC, Frisco S, et al. Li_2O -based cathode additives enabling prelithiation of Si anodes. *Appl Sci.* 2021;11(24):12027.
- Solchenbach S, Wetjen M, Pritzl D, Schwenke KU, Gasteiger HA. Lithium oxalate as capacity and cycle-life enhancer in LNMO/graphite and LNMO/SiG full cells. *J Electrochem Soc.* 2018;165(3):A512-A524.
- Zou K, Song Z, Gao X, et al. Molecularly compensated premetallation strategy for metal-ion batteries and capacitors. *Angew Chem Int Ed.* 2021;60(31):17070-17079.
- 73. Sun Y, Lee HW, Zheng G, et al. In situ chemical synthesis of lithium fluoride/metal nanocomposite for high capacity prelithiation of cathodes. *Nano Lett.* 2016;16(2):1497-1501.
- Sun Y, Lee HW, Seh ZW, et al. High-capacity battery cathode prelithiation to offset initial lithium loss. *Nat Energy*. 2016;1(1):15008.
- Du J, Wang W, Sheng Eng AY, et al. Metal/LiF/Li₂O nanocomposite for battery cathode prelithiation: trade-off between capacity and stability. *Nano Lett.* 2020;20(1):546-552.
- Rao Z, Wu J, He B, et al. A prelithiation separator for compensating the initial capacity loss of lithium-ion batteries. ACS Appl Mater Interfaces. 2021;13(32):38194-38201.
- 77. Zheng J, Liang K, Shi K, Qiu Y. In situ synthesis and electrochemical properties of Fe/Li₂O as a high-capacity cathode prelithiation additive for lithium ion batteries. *Int J Electrochem Sci.* 2016;14(6):5305-5316.
- 78. Sun Y, Lee HW, Seh ZW, et al. Lithium sulfide/metal nanocomposite as a high-capacity cathode prelithiation material. *Adv Energy Mater*. 2016;6(12):1600154.
- Shellikeri A, Watson VG, Adams DL, et al. Pre-lithiation of carbon anodes using different lithium-sources. *ECS Trans.* 2017;77(11):293-303.
- Kulova TL, Skundin AM. Irreversible capacity elimination via immediate contact of carbon with lithium metal. J Solid State Electrochem. 2003;8(1):59-65.
- Zhang X, Fan C, Han S. Improving the initial coulombic efficiency of hard carbon-based anode for rechargeable batteries with high energy density. *J Mater Sci.* 2017;52(17): 10418-10430.
- Ming J, Kwak WJ, Youn SJ, Ming H, Hassoun J, Sun YK. Lithiation of an iron oxide-based anode for stable, highcapacity lithium-ion batteries of porous carbon-Fe₃O₄/Li [Ni_{0.59}Co_{0.16}Mn_{0.25}]O₂. Energy Technol. 2014;2(9-10):778-785.
- Chen H, Yang Y, Boyle DT, et al. Free-standing ultrathin lithium metal–graphene oxide host foils with controllable thickness for lithium batteries. *Nat Energy*. 2021;6(8):790-798.
- Yue XY, Yao YX, Zhang J, et al. Unblocked electron channels enable efficient contact prelithiation for lithium-ion batteries. *Adv Mater*. 2022;34(15):2110337.
- 85. Wang H, Zhang M, Jia Q, et al. Exploiting the capacity merits of Si anodes in the energy-dense prototypes via a homogeneous prelithiation therapy. *Nano Energy*. 2022;95:107026.

- Okubo T, Saito M, Yodoya C, et al. Effects of Li pre-doping on charge/discharge properties of Si thin flakes as a negative electrode for Li-ion batteries. *Solid State Ionics*. 2014;262:39-42.
- 87. Meng Q, Li G, Yue J, Xu Q, Yin YX, Guo YG. Highperformance lithiated SiO_x anode obtained by a controllable and efficient prelithiation strategy. *ACS Appl Mater Interfaces*. 2019;11(35):32062-32068.
- Bärmann P, Diehl M, Göbel L, et al. Impact of the silicon particle size on the pre-lithiation behavior of silicon/carbon composite materials for lithium ion batteries. *J Power Sources*. 2020;464:228224.
- Liu N, Hu L, McDowell MT, Jackson A, Cui Y. Prelithiated silicon nanowires as an anode for lithium ion batteries. *ACS Nano*. 2011;5(8):6487-6493.
- Shen C, Fu R, Xia Y, Liu Z. New perspective to understand the effect of electrochemical prelithiation behaviors on silicon monoxide. *RSC Adv.* 2018;8(26):14473-14478.
- 91. Adhitama E, Dias Brandao F, Dienwiebel I, et al. Prelithiation of silicon anodes by thermal evaporation of lithium for boosting the energy density of lithium ion cells. *Adv Funct Mater.* 2022;32(22):2201455.
- Sugiawati VA, Vacandio F, Yitzhack N, Ein-Eli Y, Djenizian T. Direct pre-lithiation of electropolymerized carbon nanotubes for enhanced cycling performance of flexible Li-ion micro-batteries. *Polymers*. 2020;12(2):406.
- Lee S, Song H, Hwang JY, Jeong Y. Directly-prelithiated carbon nanotube film for high-performance flexible lithiumion battery electrodes. *Fibers Polym.* 2017;18(12):2334-2341.
- Kim HJ, Choi S, Lee SJ, et al. Controlled prelithiation of silicon monoxide for high performance lithium-ion rechargeable full cells. *Nano Lett.* 2016;16(1):282-288.
- Cao Z, Xu P, Zhai H, et al. Ambient-air stable lithiated anode for rechargeable Li-ion batteries with high energy density. *Nano Lett.* 2016;16(11):7235-7240.
- Jarvis CR, Lain MJ, Yakovleva MV, Gao Y. A prelithiated carbon anode for lithium-ion battery applications. *J Power Sources*. 2006;162(2):800-802.
- Jarvis CR, Lain MJ, Gao Y, Yakovleva M. A lithium ion cell containing a non-lithiated cathode. *J Power Sources*. 2005; 146(1-2):331-334.
- 98. Yersak TA, Son SB, Cho JS, et al. An all-solid-state Li-ion battery with a pre-lithiated Si-Ti-Ni alloy anode. *J Electrochem Soc.* 2013;160(9):A1497-A1501.
- 99. Zhao H, Wang Z, Lu P, et al. Toward practical application of functional conductive polymer binder for a high-energy lithium-ion battery design. *Nano Lett.* 2014;14(11):6704-6710.
- 100. Wang Z, Fu Y, Zhang Z, et al. Application of stabilized lithium metal powder (SLMP[®]) in graphite anode—a high efficient prelithiation method for lithium-ion batteries. *J Power Sources*. 2014;260:57-61.
- 101. Pan Q, Zuo P, Mu T, et al. Improved electrochemical performance of micro-sized SiO-based composite anode by prelithiation of stabilized lithium metal powder. *J Power Sources*. 2017;347:170-177.
- 102. Tahir MS, Weinberger M, Balasubramanian P, et al. Silicon carboxylate derived silicon oxycarbides as anodes for lithium ion batteries. *J Mater Chem A*. 2017;5(21):10190-10199.
- 103. Forney MW, Ganter MJ, Staub JW, Ridgley RD, Landi BJ. Prelithiation of silicon-carbon nanotube anodes for lithium

ion batteries by stabilized lithium metal powder (SLMP). Nano Lett. 2013;13(9):4158-4163.

104. Li Y, Fitch B. Effective enhancement of lithium-ion battery performance using SLMP. *Electrochem Commun.* 2011;13(7): 664-667.

CARBON ENERGY-WILEY

- Wang L, Fu Y, Battaglia VS, Liu G. SBR-PVDF based binder for the application of SLMP in graphite anodes. *RSC Adv.* 2013;3(35):15022-15027.
- 106. Ai G, Wang Z, Zhao H, et al. Scalable process for application of stabilized lithium metal powder in Li-ion batteries. *J Power Sources*. 2016;309:33-41.
- 107. Seong IW, Kim KT, Yoon WY. Electrochemical behavior of a lithium-pre-doped carbon-coated silicon monoxide anode cell. J Power Sources. 2009;189(1):511-514.
- Li X, Li Y, Tang Y, Zhang L, Huang J. Air stable lithium microspheres prelithiation reagents for Li-ion batteries synthesized via electroplating. *J Power Sources*. 2021;496:229868.
- 109. Yang SY, Yue XY, Xia HY, et al. Battery prelithiation enabled by lithium fixation on cathode. *J Power Sources*. 2020;480:229109.
- Zhan Y, Yu H, Ben L, et al. Application of Li₂S to compensate for loss of active lithium in a Si-C anode. *J Mater Chem A*. 2018;6(15):6206-6211.
- 111. Zhan Y, Yu H, Ben L, Chen Y, Huang X. Using Li_2S to compensate for the loss of active lithium in Li-ion batteries. *Electrochim Acta*. 2017;255:212-219.
- 112. Liu Z, Ma S, Mu X, Li R, Yin G, Zuo P. A scalable cathode chemical prelithiation strategy for advanced silicon-based lithium ion full batteries. *ACS Appl Mater Interfaces*. 2021; 13(10):11985-11994.
- 113. Scott MG, Whitehead AH, Owen JR. Chemical formation of a solid electrolyte interface on the carbon electrode of a Li-ion cell. *J Electrochem Soc.* 1998;145(5):1506-1510.
- 114. Tabuchi T, Yasuda H, Yamachi M. Li-doping process for Li_xSiOnegative active material synthesized by chemical method for lithium-ion cells. *J Power Sources*. 2005;146(1-2):507-509.
- 115. Yoshida S, Masuo Y, Shibata D, Haruta M, Doi T, Inaba M. Li pre-doping of amorphous silicon electrode in Li-naphthalene complex solutions. *Electrochemistry*. 2015;83(10):843-845.
- 116. Shen Y, Qian J, Yang H, Zhong F, Ai X. Chemically prelithiated hard-carbon anode for high power and high capacity Li-ion batteries. *Small.* 2020;16(7):1907602.
- 117. Shen Y, Zhang J, Pu Y, et al. Effective chemical prelithiation strategy for building a silicon/sulfur Li-ion battery. ACS Energy Lett. 2019;4(7):1717-1724.
- 118. Wang G, Li F, Liu D, et al. Chemical prelithiation of negative electrodes in ambient air for advanced lithium-ion batteries. *ACS Appl Mater Interfaces*. 2019;11(9):8699-8703.
- 119. Jang J, Kang I, Choi J, et al. Molecularly tailored lithium–arene complex enables chemical prelithiation of high-capacity lithium-ion battery anodes. *Angew Chem Int Ed.* 2020;59(34):14473-14480.
- 120. Shen Y, Shen X, Yang M, et al. Achieving desirable initial coulombic efficiencies and full capacity utilization of Li-ion batteries by chemical prelithiation of graphite anode. *Adv Funct Mater.* 2021;31(24):2101181.
- 121. Choi J, Jeong H, Jang J, et al. Weakly solvating solution enables chemical prelithiation of graphite-SiO_x anodes for high-energy Li-ion batteries. *J Am Chem Soc.* 2021;143(24): 9169-9176.

- 122. Liu X, Tan Y, Liu T, et al. A simple electrode-level chemical presodiation route by solution spraying to improve the energy density of sodium-ion batteries. *Adv Funct Mater*. 2019;29(50):1903795.
- 123. Li Y, Qian Y, Zhao Y, Lin N, Qian Y. Revealing the interfacerectifying functions of a Li-cyanonaphthalene prelithiation system for SiO electrode. *Sci Bull.* 2022;67(6):636-645.
- 124. Zhang X, Qu H, Ji W, et al. Fast and controllable prelithiation of hard carbon anodes for lithium-ion batteries. *ACS Appl Mater Interfaces*. 2020;12(10):11589-11599.
- 125. Li F, Wang G, Zheng D, et al. Controlled prelithiation of SnO₂/C nanocomposite anodes for building full lithium-ion batteries. ACS Appl Mater Interfaces. 2020;12(17):19423-19430.
- 126. Inamoto J, Maruyama S, Matsuo Y, Uchida S, Maeda K, Ishikawa M. Effects of pre-lithiation on the electrochemical properties of graphene-like graphite. *Electrochemistry*. 2019; 87(5):260-264.
- 127. Holtstiege F, Koç T, Hundehege T, Siozios V, Winter M, Placke T. Toward high power batteries: pre-lithiated carbon nanospheres as high rate anode material for lithium ion batteries. *ACS Appl Energy Mater.* 2018;1(8):4321-4331.
- 128. Wu H, Zheng L, Zhan J, et al. Recycling silicon-based industrial waste as sustainable sources of Si/SiO₂ composites for high-performance Li-ion battery anodes. *J Power Sources*. 2020;449:227513.
- 129. Li X, Liang J, Hou Z, et al. The design of a high-energy Li-ion battery using germanium-based anode and LiCoO₂ cathode. *J Power Sources*. 2015;293:868-875.
- Guo A, Chen E, Heller A, Mullins CB. Controlled prelithiation of PbS to Pb/Li₂S for high initial Coulombic efficiency in lithium ion batteries. *J Electrochem Soc.* 2019;166(10):A1939-A1943.
- 131. Wang F, Wang B, Yu Z, et al. Construction of air-stable prelithiated SiO_x anodes for next-generation high-energy-density lithium-ion batteries. *Cell Rep Phys Sci.* 2022;3(5):100872.
- 132. Palanisamy M, Parekh MH, Pol VG. In situ replenishment of formation cycle lithium-ion loss for enhancing battery life. *Adv Funct Mater.* 2020;30(46):2003668.
- 133. Zhou H, Wang X, Chen D. Li-metal-free prelithiation of Si-based negative electrodes for full Li-ion batteries. *ChemSusChem.* 2015;8(16):2737-2744.
- 134. de La Llave E, Borgel V, Park KJ, et al. Comparison between Na-ion and Li-ion cells: understanding the critical role of the cathodes stability and the anodes pretreatment on the cells behavior. *ACS Appl Mater Interfaces*. 2016;8(3):1867-1875.
- 135. Watanabe T, Tsuda T, Ando N, et al. An improved prelithiation of graphite anodes using through-holed cathode and anode electrodes in a laminated lithium ion battery. *Electrochim Acta*. 2019;324:134848.
- Yu L, Tian Y, Xiao X, et al. Investigation on the overlithiation mechanism of LiCoO₂ cathode for lithium ion batteries. *J Electrochem Soc.* 2021;168(5):050516.
- 137. Aravindan V, Nan S, Keppeler M, Madhavi S. Pre-lithiated $Li_xMn_2O_4$: a new approach to mitigate the irreversible capacity loss in negative electrodes for Li-ion battery. *Electrochim Acta*. 2016;208:225-230.
- 138. Song Z, Feng K, Zhang H, et al. "Giving comes before receiving": high performance wide temperature range Li-ion battery with $\text{Li}_5\text{V}_2(\text{PO}_4)_3$ as both cathode material and extra Li donor. *Nano Energy*. 2019;66:104175.

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 Mate-

rials 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

CARBON ENERGY-WILEY

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.

How to cite this article: Chen S, Wang Z, Zhang M, et al. Practical evaluation of prelithiation strategies for next-generation lithium-ion batteries. *Carbon Energy*. 2023;e232. doi:10.1002/cey2.323

on Wiley Online Library for rules

use; OA articles

are governed by the applicable Creative