Chemical Engineering Journal 493 (2024) 152542

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Active prelithiation strategies for advanced lithium storage systems: A perspective from electrochemical mechanism to structural design and application

Bo Jin [a,b], Keyu Zhang [a,b,*], Geng Gao [a,b], Qing Zhao [a,b], Xinyu Jiang [a,b], Dingfang Cui [a,c], Keqi Chen [a,b], Xiang Lin [a,b], Liuliu Liu [a,b], Rui Yan [a,b], Bin Yang [a], Yaochun Yao [a,b,*]

[a] *National Engineering Research Center of Vacuum Metallurgy, Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China*
[b] *National Local Joint Engineering Laboratory of Lithium Ion Battery and Material Preparation Technology, Kunming University of Science and Technology, Kunming 650093, China*
[c] *Yunnan Chihong International Germanium Industry Co., Ltd., Qujing 655011, China*

ARTICLE INFO

Keywords:
Prelithiation
Structural design
Electrochemical mechanism
Commercial application

ABSTRACT

Given the rising demand for high-energy–density devices in the commercial market, exploring new electrode materials is crucial for enhancing the energy density of lithium-ion batteries (LIBs). Novel electrode materials, which rely on conversion and alloy reactions, have attracted attention due to their high specific capacity and abundant resources. However, these materials often suffer from a large initial irreversible capacity and low-capacity retention, leading to significant active lithium consumption and a reduction in overall battery energy density. Consequently, a concise and efficient prelithiation technique is urgently needed to improve their electrochemical performance for commercial applications. Although various prelithiation methods have been developed, they predominantly remain experimental due to issues such as high reduction potential, poor prelithiation accuracy, and incompatibility with electrolytes, among others. From an industrial perspective, understanding the electrochemical reaction mechanisms and designing effective prelithiation technologies and electrode structures are vital for advanced lithium storage systems. This review first discusses the causes of active lithium loss and the electrochemical reaction mechanisms of different prelithiation methods. It summarizes the applications of advanced characterization methods in prelithiation technology. Then, various prelithiation strategies are reviewed and generalized according to the different components of LIBs. Additionally, the review examines the pathways for lithium replenishment and the recent developments in electrode structures within prelithiation strategies. Finally, the future perspectives and challenges of prelithiation technology in commercial applications are analyzed and projected.

1. Introduction

As the demand for high energy and power density, long cycling life, fast charging, safety, and durability in electric vehicles and portable electronics grows, traditional secondary batteries (such as lead-acid batteries and nickel-cadmium batteries) are being phased out due to their short lifespan and environmental impact. Consequently, the exploration of high-energy–density lithium-ion batteries (LIBs) has become a prominent field of research [1–8]. The lower theoretical energy densities of commercialized cathodes (such as $LiNi_xCo_yMn_zO_2$, $LiNi_xCo_yAl_zO_2$, $LiCoO_2$, and $LiFePO_4$) and graphite anodes currently limit the enhancement of the overall energy density of LIBs [9–12]. To significantly increase the energy density of these devices, it has been technically challenging without replacing the existing electrode system. In recent years, improvements in the actual energy density of LIBs have been achieved primarily by enhancing the overall mass share of cathode and anode active substances in the batteries [13,14]. Therefore, there is a pressing need to research high-capacity, safe, and stable electrode materials to replace the current ones and improve the energy density of LIBs.

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* Corresponding authors at: National Engineering Research Center of Vacuum Metallurgy, Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China.
E-mail addresses: lkdzky@163.com (K. Zhang), yaochun9796@163.com (Y. Yao).

https://doi.org/10.1016/j.cej.2024.152542
Received 6 April 2024; Received in revised form 18 May 2024; Accepted 24 May 2024
Available online 25 May 2024

Currently, lithium storage mechanisms allow for the classification of various high-capacity electrode materials into three types: alloying-type, intercalation-type, and conversion-reaction-type [15,16]. Among these, alloying-type anode materials include silicon-carbon, tin-based, germanium-based, and phosphorus-based materials. These materials are known for their higher specific capacity, lower cost, and enhanced safety [17–21]. However, they suffer from significant volumetric changes during charging and discharging, which lead to electrode damage and poor cycling performance. Moreover, the unstable volumetric effects in alloyed materials result in the repeated formation of solid electrolyte interfaces (SEI) at the particle interfaces, causing higher irreversible lithium losses [22]. Transition metal oxides, transition metal oxalates, and other conversion-responsive anode materials display excellent rate performance, higher specific capacities, and low costs [23]. Despite these advantages, they possess high irreversible capacities during initial charge–discharge cycles and exhibit poor cycling stability. This issue is primarily attributed to the low electrochemical activity of the conversion reaction products and the deposition of irreversible lithium sources on the particle surfaces, forming “organic” layers and SEI films due to electrolyte decomposition during cycling [24–26]. The common inherent defects, notably the irreversible lithium loss in these new energy materials, manifest as significant initial irreversible capacity, poor cycling performance, and reduced service life in battery assemblies. This contradicts the original goal of developing new anode materials to enhance battery energy density. Consequently, addressing the initial capacity loss in new anode materials is crucial for improving the energy density of LIBs. Prelithiation technology involves introducing lithium-rich additives to electrode materials or employing chemical/electrochemical reactions to compensate for the irreversible lithium loss caused by SEI formation during initial cycling and the incomplete lithiation reaction in subsequent cycles [27–29]. This strategy significantly reduces the initial reversible capacity, boosts Coulombic efficiency (CE), and ensures a continuous and stable Li ions de-intercalation process. It also stabilizes the electrode structure and enhances the diffusion coefficient of lithium ions, thus providing effective technical support for the commercialization of new high-capacity electrode materials.

In recent years, as research into the interface structure of electrodes and the transport mechanism of lithium ions in LIBs has deepened, prelithiation technology has gradually matured. This technology enhances the electrochemical stability of active materials by generating artificial SEI films [30–32]. Tailored to the specific characteristics of different electrode materials, prelithiation strategies can effectively mitigate capacity loss. They reduce the consumption of lithium sources and add lithium-rich substances only to supplement the irreversible lithium loss caused by SEI formation and the electrochemical inactivation of electrode materials, thereby achieving higher energy densities while maintaining the original structure of the electrode. Due to minimal changes in the original production processes for electrodes and devices, prelithiation strategies are particularly well-suited for large-scale commercial applications [33]. This review organizes perspectives based on the mechanism of lithium inactivation and the impact of prelithiation on electrochemical performance. It summarizes various physicochemical prelithiation strategies for different anode materials and lithium supplementation for cathode materials in recent years. Fig. 1 illustrates the theme and classifications of prelithiation methods. However, much literature focuses on prelithiation methodes or electrode structure design without addressing crucial basic scientific parameters such as the accuracy of prelithiation, lithium replenishment capacity, environmental stability of prelithiation materials/reagents, and industrial maneuverability, which are vital for practical industrial applications. In this review, we combine the latest research progress in prelithiation of LIBs with theoretical analysis and mechanism elucidation for different prelithiation methods. Additionally, we discuss the challenges currently faced by prelithiation technology and explore future development directions for potential industrial applications.

2. Lithiun inactivation and prelithiation mechanism

2.1. Lithium loss and lithium inactivation

The reduced CE of LIBs in the initial few cycles demonstrates a partial irreversible loss of Li ions during charging and discharging, leading to decreased full-cell energy density and shortened cycle life. Recent years have seen the development of novel high-energy–density electrode materials, including embedded/exfoliated, converted, and alloyed anode materials, which all offer higher capacity densities than traditional commercial graphite anode materials. However, these materials often fail to achieve satisfactory cycling performance and compatibility

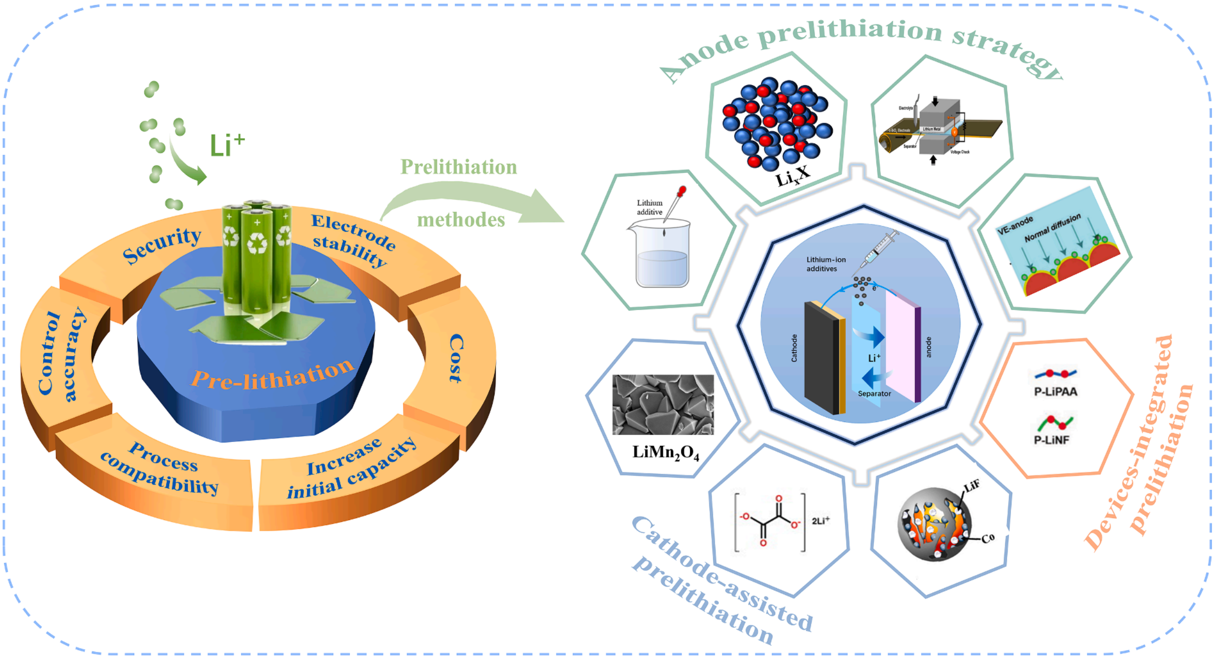


Fig. 1. Target and classification of various prelithiation methods.

with existing processes due to inherent defects that result in low initial Coulombic efficiency (ICE, typically below 80%). Understanding the failure mechanisms of active lithium in electrode materials is crucial to addressing their low CE and integration challenges. This review primarily focuses on three types of causes for lithium loss and inactivation:

1. Interfacial properties of electrodes and electrolyte decomposition: The performance of LIBs is significantly impacted by the interfacial properties of electrodes and the decomposition of electrolytes [34–38]. LIBs typically use non-aqueous liquid organic electrolytes comprised of ester organic solvents such as EC [39], DMC, and solvated lithium salts (e.g., $LiPF_6$, $LiClO_4$, LiTFSI, and $LiSO_3CF_3$). These are prone to irreversible decomposition at low potentials (0.8–2.0 V vs. Li/Li^+), leading to reactions like EC/DMC + Li^+ + e^- → SEI (Li_2CO_3/LiO_2COR (R-alkyl) where R is an alkyl group). Additionally, one or more layers of solid electrolyte interphase (SEI) will form on the anode surface, as illustrated in Fig. 2a. The lithium salt in the electrolyte plays a crucial role in the formation of the SEI, which chemically bonds with the electrode material surface to generate organic and inorganic compounds such as LiF, Li_2O_2, and Li_2O (Fig. 2b). During charging and discharging, organic solvents in the electrolyte are susceptible to dehydrogenation, cracking,

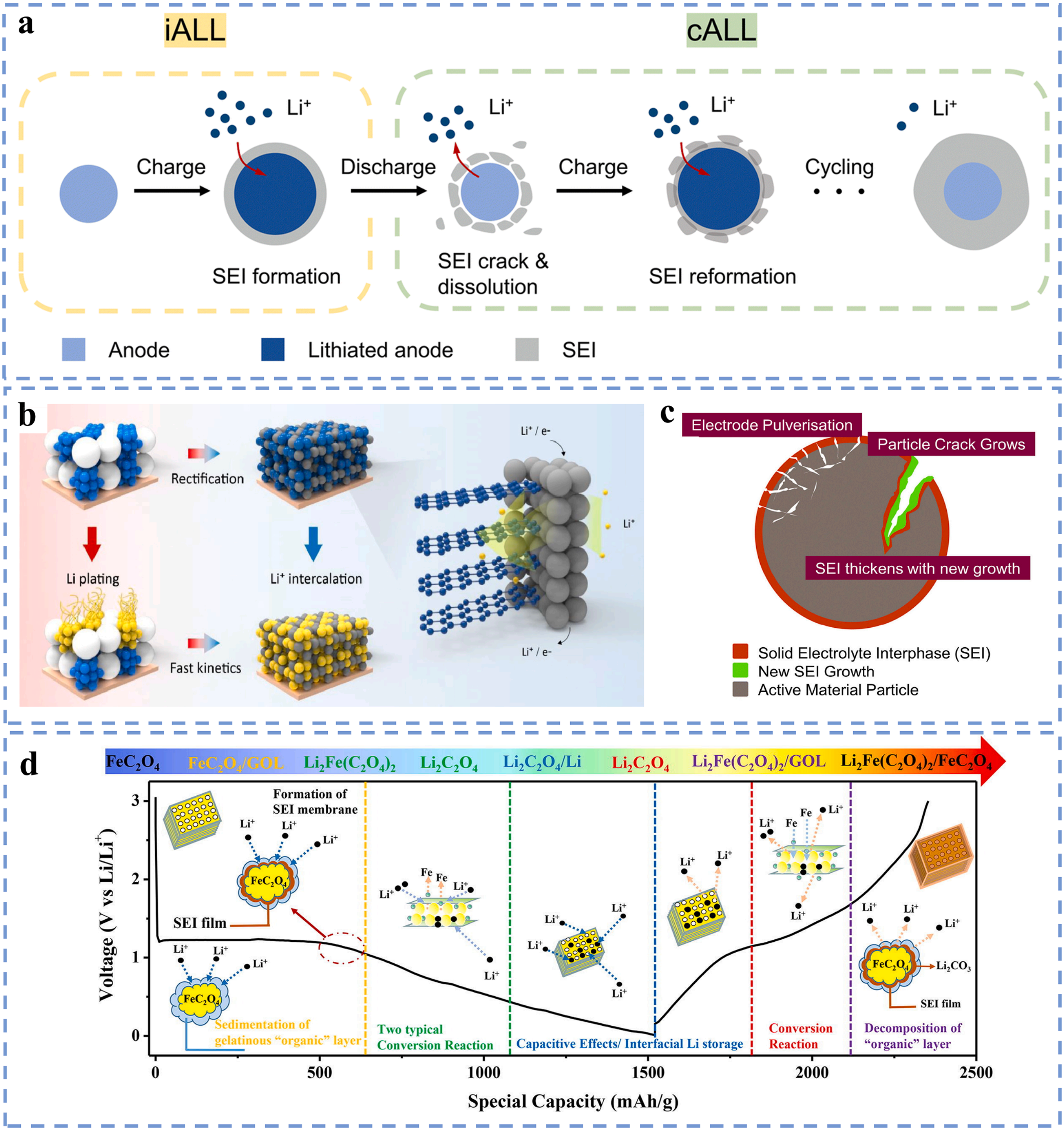


Fig. 2. Reasons for Li^+ consumption and inactivation: a) Schematic of the initial active lithium loss and continuous active lithium loss that occurs during battery cycling [44]. b) The generation progress of lithium plating on the graphite interface [44]. c) New SEI generated during the expansion of silicon anode electrodes [22]. d) Formation of intermediate phases during the conversion of iron oxalate [56].

and other reactions, producing various degradation products, such as lithium ethylene dicarbonate (LEDC) $(CH_2OCO_2Li)_2$, and polycarbonates. Small amounts of carbonate compounds, like lithium carbonate (Li_2CO_3), react with lithium on the electrode surface to form a dense carbonate SEI film. This film acts as a passivation layer on the anode surface, inhibiting further electrolyte decomposition. The continuous growth and thickening of the SEI film during cycling irreversibly consume a significant amount of lithium source, reducing the overall energy density of the battery and becoming a major source of capacity loss in the pre-cycle stage. However, a stabilized SEI can improve the interfacial properties of the electrode materials and enhance long-term cycling performance of LIBs [40–42]. Aurbach et al. [43] studied the SEI on the surfaces of lithium metal and graphite anode materials. They reported that the SEI film on lithium metal surfaces is unstable during the charging and discharging process and exhibits significant volumetric changes, which can damage the SEI film. Consequently, the exposed lithium surface interacts with the electrolyte to form a thicker SEI film, consuming a substantial amount of lithium source from the cathode during repeated charging and discharging cycles, until a more stable composition is achieved.

2. Lithium metal deposition (Lithium plating): Lithium loss in graphite-based anode materials is associated not only with the formation of the SEI but also with lithium deposition on its surface, commonly referred to as lithium plating. Lithium plating primarily occurs under conditions such as low temperatures, high charging currents, and high states of charge (SOC) [44–46]. Additionally, factors such as aging-related capacity imbalance, mechanical failures, variations in battery operating voltage, and the thickening of the SEI contribute to lithium plating at operating temperatures [47–49]. The chemical polarization of lithium ions at the electrode due to limited diffusion rates during low-temperature charging, along with electrochemical polarization caused by the accumulation of lithium ions at the SEI interface during high-current charging, results in increased polarization at the negative electrode. This leads to a reduction in the lithium-ion reduction potential. When the graphite potential drops below 0 V with respect to Li/Li^+, lithium plating occurs. The spontaneous reaction of lithium metal with the electrolyte forms a passivation layer, increasing the electrode's impedance. Not only does lithium plating cause significant capacity degradation and reduced ICE, but it also poses serious safety hazards due to increased electrochemical impedance.

3. Structural destruction during lithiation: During the lithiation process, certain anode materials undergo structural destruction, leading to the electrochemical inactivation of active substances and the repeated formation of an unstable SEI film. Notably, silicon-based materials exhibit abnormal expansion effects, expanding up to three times their original volume [50–52] (Fig. 2c). As lithium embeds into the Si anode, it forms $Li_{15}Si_4$ and $Li_{22}Si_5$ alloys, which undergo this significant expansion, inevitably causing the Si-based anode material to crack or powder [52,53]. As Li ions diffuse into the vicinity of these damaged structures, they become trapped, leading to the continuous formation of new SEI and the consequent consumption of a portion of the lithium during each cycle. In carbon-silicon composites, silicon particles are often encapsulated within a carbon shell. This core–shell structure can break away during battery cycling, a phenomenon known as "flaking." This leads to capacity loss and loosening of the electrode structure. All these factors contribute to a gradual loss of capacity during cycling.

4. Lower electrochemical activity of anode materials: The lower electrochemical activity of anode materials during the lithiation/delithiation process contributes to the practical irreversibility of lithium ions [54]. Diverse lithium storage materials can offer higher energy densities due to a wide range of lithium storage reactions. However, these multiple reactions can also lead to poorer reactivity, primarily affected by ion and electron migration, and the activation energy of interfacial reactions. The slow kinetic release of lithium ions in the electrolyte, the formation of stable alloy compounds after reduction reactions, and strong bonding with fewer ligand atoms at defective sites of anode materials lead to the depletion of lithium ions in the anode. Furthermore, based on the transformation reaction (an undesirable irreversible side reaction) for transition metal oxides or oxygenated materials, the generated metal nanoparticles tend to aggregate, reducing the overall electrochemical activity of the material. This aggregation results in the decomposition of lithium salts and the detachment of lithium ions [55]. For example, Zhang et al. [56] reported that iron oxalate electrodes generated an organic layer and an intermediate compound $Li_2Fe(C_2O_4)_2$ (Fig. 2d) during initial lithiation, instead of directly forming lithium oxalate and iron nanoparticles. This organic layer and the intermediate compound, possessing low electrochemical activity, consume some lithium ions, leading to a decrease in the battery's reversible capacity.

2.2. Prelithiation mechanism

Prelithiation is an effective method to compensate for the irreversible capacity loss that occurs during the initial battery cycle. However, the mechanisms of prelithiation, such as the formation of the solid-electrolyte interface (SEI) and "lithium capture" by conversion-reactive materials, remain poorly understood. Furthermore, the utilization rate of lithium sources for prelithiation is low (<65%), and most prelithiation processes are still confined to laboratory stages, with large-scale commercial application yet to be realized. It is crucial to study the electrochemical reactions and the evolution of products at the Li source/anode interface, as well as to analyze the impacts of electron channels, interface composition, and Li-ions diffusion channels on the prelithiation of electrodes.

In exploring various prelithiation mechanisms, the diffusion steps of Li-ions through the SEI and the dynamics of Li-ions diffusion channels can be calculated using DFT. This aids in analyzing the subsequent potential gradient and stress field distribution at the interface, which are vital for the kinetic analysis of Li-ions diffusion. Moreover, employing advanced characterization tools significantly enhances the analysis of interface evolution. Techniques such as in situ scanning electron microscopy allow for dynamic analysis of the surface morphology to assess the degree of prelithiation. High-magnification transmission electron microscopy can observe changes in the thickness of the active lithium metal layer and SEI and analyze the composition of various lithium alloying compounds. TOF-SIMS is useful for analyzing the distribution of trace lithium on the electrode surface, thereby verifying the homogeneity of prelithiation [98]. Additionally, three-dimensional atomic force microscopy (3D-AFM) can examine the effects of interface roughness and the deformation of the lithium film post-prelithiation. Other conventional characterization tools such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) analysis [121], and Raman spectroscopy are employed to jointly confirm the interfacial evolution before and after prelithiation and to elucidate the reaction mechanisms of different prelithiation techniques. Table 1 displays several prevalent characterisation tools employed in prelithiation techniques for LIBs. In conclusion, the prelithiation strategy aims to maintain a high number of active Li ions throughout the battery process and to consciously develop a uniform and stable SEI layer, ensuring the full utilization of the lithium source from the cathode material.

Based on the variations in lithium loss and deactivation across different electrode materials, prelithiation mechanisms can be broadly categorized as follows:

1. Constructing an irreversible lithium source for the anode material before electrochemical cycling: Due to the decomposition of the electrolyte at low potentials, an SEI film, either fully or partially formed in advance at the interface between the anode electrode and electrolyte, plays a crucial role in stabilizing the electrode and compensating for lithium loss through the prelithiation process. This mechanism establishes an irreversible lithium source on the anode electrode beforehand, which reduces the irreversibility of Li ions from the anode during the

Table 1
Common characterization tools for LIBs prelithiation technology.

Application direction	Instruments	Application	Ref.
Component characterization	ICP-OES	Measurement of electrode materials for major, minor and trace elements	[101]
	SIMS	the longitudinal distribution of the composition of the electrode	[102]
	XPS	Determination of the constituent elements and chemical state of the electrode surface	[58,86]
	EELS	Measuring the elemental composition, chemical bonding, and electronic structure of electrode materials	[59]
	STXM	Enabling non-destructive 3D imaging of electrode materials	[60]
	XANES	Charge transfer analysis of atoms	[61]
	XRF	Principal component and impurity element analysis of electrode materials	[62]
Morphology characterization	SEM	Characterize the surface topography and roughness of the sample	[109]
	TEM	Measuring morphology and lattice fringing at interfaces	[110]
	AFM	Flatness analysis of nanomaterial surfaces	[98]
Crystal structure characterization	XRD	Crystal structure analysis of common electrode materials	[121]
	EXAFS	Measurement of the crystal structure of atoms with less than wt 1 %	[63]
	Neutron diffraction	Observation of the crystal structure and arrangement of larger radius atoms	[64]
	NMR	Detection of dendritic and intra-particle phase transition reactions and determination of lithium self-diffusion coefficients	[65]
	STEM	Observation of the arrangement of atoms, the lattice of atoms and atomic occupation	[98]
	Raman	Characterization of graphitized carbon materials	[66]
Characterization of functional groups	Raman spectra	Characterization of the evolution of certain compounds during charging and discharging processes	[57]
	FITR	Evolution of characteristic functional groups in materials	[92]
Mechanical measurement	SPM Probe	Mechanical characterization of SEI membranes	[69]
Interfacial Potential Measurement	KPFM	Measurement of the potential distribution on the electrode surface	[67]
	PEEM	Measurement of the potential distribution on the electrode surface	[68]

charging and discharging processes of the battery, thereby enhancing the overall cycle efficiency of the battery (Fig. 3a). Yang et al. [70] developed a roll-to-roll transfer process for the continuous prelithiation of LIBs anodes, providing a highly efficient and controllable lithium source for SEI film generation in graphite and silicon/carbon composite electrodes. It was observed that the ICE of the half-cells reached 99.99% and 99.05%, respectively. Furthermore, the ICE and energy densities of the full cells showed significant improvement with the electrode prelithiation, suggesting that the lithium loss, rooted in electrolyte decomposition and other factors, can be significantly mitigated by adding an irreversible lithium source.

2. Constructing a reversible lithium source inside the anode material: During initial cycling, many Li ions around the positive electrode undergo secondary reactions in the anode electrode, producing a product with lower electrochemical activity. In subsequent cycles, these Li-ions cannot detach from the anode electrode to rejoin the positive electrode, resulting in a lower CE. From the perspective of the "rocking chair" migration of Li ions between the anode and cathode, adding a reversible lithium source to the anode material in advance can replace the irreversible lithium loss, ensuring the number of Li ions migrating back to the cathode, thus stabilizing the capacity retention rate and CE of LIBs. Adding a precise amount of stabilized lithium metal powder (SLMP) or lithium-rich compounds to the anode is currently the mainstream method (Fig. 3b). Li's group [71] demonstrated that adding SLMP significantly enhanced the irreversible capacity of graphite/spinel $LiMn_2O_4$ batteries. The ICE with SLMP addition in the first cycle increased from 82% to 91% in the control group, and the irreversible capacity of the half-battery was significantly reduced in subsequent cycles. Moreover, the SLMP helped deplete water and other acidic impurities in the battery system, improving the cycling stability of the electrodes.

3. Constructing an irreversible lithium source inside the cathode material (as shown in Fig. 3c): Lithium loss in this context refers to a state where Li ions are not fully embedded after being released from the cathode material in the context of a full battery. During the material synthesis process, an irreversible source of lithium can be introduced into the cathode. This source can decompose at high potentials, facilitating the movement of Li ions to the anode electrode, forming inactivated lithium salts in advance, and ensuring the reversibility of the lithium source in subsequent cathode materials. Lee et al. [72] used Li_2NiO_2 with an orthorhombic crystal system structure as an anode additive. The initial discharge specific capacity of the battery did not decrease significantly after the addition of 9% Li_2NiO_2 additive. This suggests that the decomposition of Li_2NiO_2 is an important factor in replenishing lithium loss from the anode material. Moreover, the decomposition reaction of Li_2NiO_2 provides over-discharge protection for the battery without affecting its other properties.

3. Anode prelithiation strategy

Currently, the most promising candidates for next-generation anode materials are conversion-type and alloy-type materials, known for their high specific capacities. However, their high irreversible capacities and the formation of a SEI film diminish the overall energy density and lifespan of the battery. The formation of an SEI film around the anode interface is inevitable, typically comprising compounds such as LiF, Li_2CO_3, Li_xPF_y, and alkyl lithium carbonate [73]. The anode material not only consumes a significant amount of lithium but also loses a substantial amount due to volume expansion and capture. The prelithiation strategy aims to compensate for these lithium losses.

3.1. Lithium metal contact prelithiation

Lithium metal can be added to the anode electrode through various physical methods—such as high temperature, high pressure, ball milling, and vaporization—and other auxiliary methods to increase the depth of lithium embedding and improve its uniformity.

3.1.1. Lithium foil contact prelithiation

A highly effective and convenient methode for replenishing lithium involves direct contact between lithium foil and the surface of anode materials, allowing for a self-discharge reaction in the electrolyte. The potential difference between the lithium foil and the anode accelerates the prelithiation reaction. After a period of self-discharge, the reaction products deposit on the anode surface, forming an SEI film. This significantly reduces the consumption of lithium from the cathode

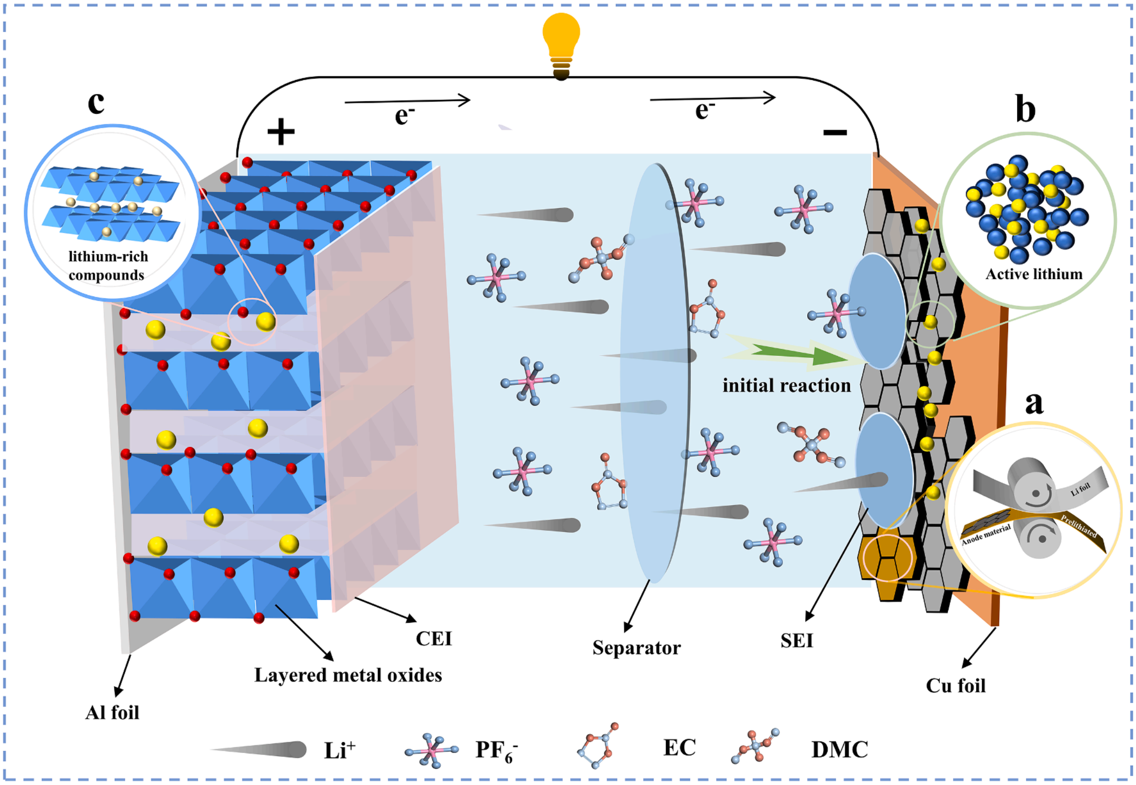


Fig. 3. The diagram of Li ions and electron transfer during the initial discharge process and three main mechanisms of prelithiation: a) Prelithiation at the anode interface. b) Adding lithium-containing additives inside of the anode electrode. c) Adding lithium-rich additives inside of the cathode electrode.

source during subsequent cycles. Liu et al. [74] utilized the self-discharge mechanism between lithium foils and anode to prelithiate silicon nanowires (SiNWs) anode, which facilitated the growth of SiNWs on stainless steel sheets in direct contact with lithium foil. They reported that after 20 min of prelithiation, the SiNWs loaded 50% of the full capacity of lithium foil (~2000 mAh g^{-1}) without any structural changes after prelithiation (Fig. 4a).

The prelithiation processes for anode materials in direct contact with lithium metal have also been reported in other studies, including those involving carbon nanotubes [75,76], porous carbon [77,78], and carbon/MoS_2 [79], among other anode materials. These methods are straightforward and directly utilize the self-discharge effect of lithium foil for prelithiation. Furthermore, the degree of prelithiation can be controlled by adjusting the reaction time based on the amount of irreversible capacity loss of the anode. However, the uneven distribution of contact points between anode materials and lithium foil results in heterogeneous lithiation, diverse lithium salts, and an unstable interface. Additionally, an excess lithium source during the reaction process can lead to the accumulation of unreacted Li^+ (dead Li) around the electrode interface, which impedes the charge-transfer reaction.

Although lithium foil prelithiation helps stabilize the migration of reversible lithium sources to some extent, it is challenging to quantitatively calculate the irreversible loss of lithium in the electrode material. This complexity makes it difficult to effectively control the addition of lithium foil and the depth of lithium replenishment. Currently, this issue can be addressed by adding a resistive buffer layer. The polymer protective layer effectively regulates the transport of lithium ions and the rate of lithiation. Meng et al. [80] inserted a resistive buffer layer (RBL) (Fig. 4b) between the lithium foil and the electrolyte to regulate the rate and degree of prelithiation. The high conductivity and porous structure of the RBL facilitate the transport of Li-ions and electron transfer. Additionally, the flexible carbon nanotubes in the RBL bring the lithium foil into close contact with the anode electrode, effectively achieving uniform prelithiation of the SiO_x anode. The use of an RBL significantly improves the lithiation uniformity by regulating the interfaces between Li^+, electrons, and the SiO_x anode.

The prelithiation process requires an inert atmosphere due to the low potential of the prelithiation reagent and its high chemical reactivity with oxygen and water. This requirement adds complexity to the process. Lee et al. [81] utilized a constant resistance short circuit (PLSC) process to pre-lithiate SiO_x electrodes (Fig. 4c). The lithiated SiO_x electrodes demonstrated superior cycle life compared to those prepared by normal discharge, retaining 88.6% of their capacity over 500 cycles. Moreover, the PLSC process significantly enhanced the energy capacity of SiO_x, with 66.6% capacity retention at 3 A g^{-1} (compared to the capacity measured at 0.1 A g^{-1}). By controlling the reaction time, an SEI layer was successfully formed on the surface of the SiO_x electrode without vacancies and boundaries, demonstrating the feasibility of the PLSC process. Cao et al. [82] developed a three-layer structured electrode (Fig. 4d) consisting of active material, polymer, and lithium anode electrode. The polymer layer protects the lithium from O_2 and moisture, maintaining material stability in 10%-30% air humidity. The polymer layer dissolves into the electrolyte, allowing the active material and lithium to form a lithiated anode after assembling the battery. This prelithiation strategy achieves an ICE of 99.7% in graphite anodes and over 100% in nano-silicon anodes, demonstrating excellent prelithiation performance. Furthermore, during the prelithiation process using lithium foil, alloying/transformation reactions between lithium metal and anode materials, along with the capacitive effect, can cause the electrode to swell and reduce overall stability.

To prevent electrode breakage and pulverization during subsequent cycling, micron-thick lithium foils containing nanocrystalline grains can be manufactured to enhance the mechanical properties of the lithium foils. Chen et al. [83] synthesized ultrathin lithium foils (0.5–20 μm) on graphene oxide substrates by injecting molten lithium metal into substrates with adjustable submicrometer thickness. Due to the 3D body structure of the substrate, lithium foils synthesized on graphene oxide exhibited greater mechanical strength than conventional lithium foils.

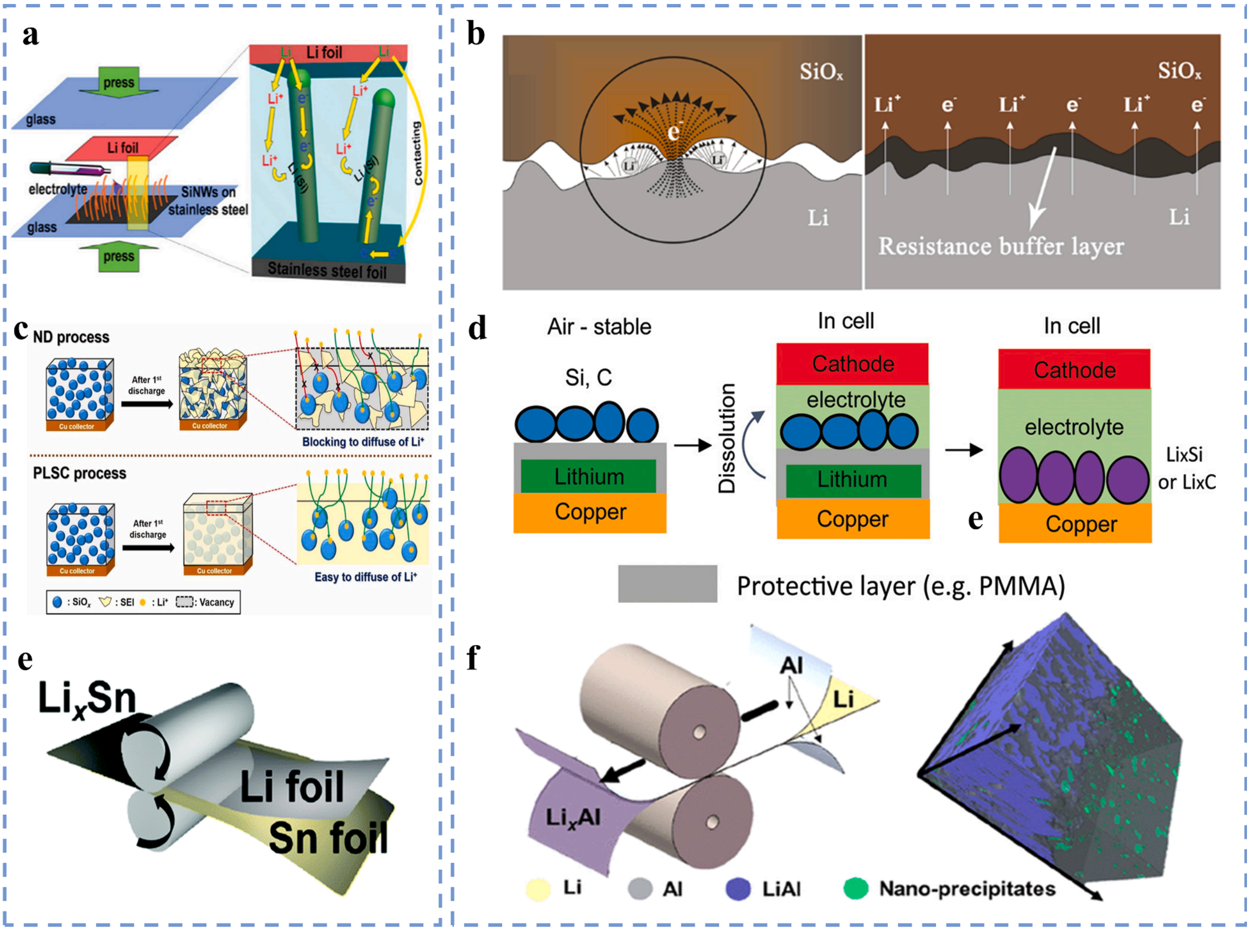


Fig. 4. A) prelithiation of silicon nanowires (sinws) on stainless steel foil and internal Li^+ and electron transfer pathways during prelithiation [74]. b) Comparison of Li^+ diffusion and electron transfer pathways in direct contact prelithiation processes and RBL-controlled pre-lithiation processes [80]. 4c) Schematic representation of SEIs formed using the PLSC process and without it in two discharge processes [81]. d) Schematic diagram of the process used to produce stable air polymer-coated lithiated anodes [82]. e) Illustration of the roll-to-roll prelithiation process for producing Li_xSn anode electrodes [84]. f) Diagram of the process used to produce an ultrananocrystalline LiAl film by the mechanical prelithiation (MP) method [85].

This improvement prevented rapid rupture of the ultrathin Li metal anode during cycling, extending the cycle life of the LMB by a factor of nine. The active lithium compensated for the capacity loss observed in the initial cycling of graphite (93%) and Si anodes (79.4 %). Xu et al. [84] employed a roll-to-roll manufacturing process to mechanically prelithiate tin foil (Fig. 4e), which increased the ICE of the resulting Li_xSn foil from 20% to 80%. This process also improved the capacity retention of a primary battery comprising a $LiFePO_4$ cathode to 94.5% after 200 cycles at 0.3C. Similar to this process, nanocrystalline Li-Al-Mn-Si foils, where reversible Li serves as the main component [85], were induced to form nanocrystalline grains by adding a small amount of Mn or Si (Fig. 4f), as shown by the reaction equation:

$$n\ Al_{FCC} + m\ Li^+(eletrolyte) + m\ e^-(metallic) \rightarrow Li_mAl_n$$

The microstructure reveals that the small nanocrystalline grains substantially decreased the porosity of the lithium foil, reduced stress after mechanical pre-structuring, and prevented the formation of dead clusters caused by solid electrolyte rupture. This aluminum-based anode electrode exhibits excellent capacity when paired with NCM 523 and LFP cathodes. Chen et al. [86] designed a 5 μm Li-Mg-Al alloy foil to prelithiate graphite, addressing the issues of lithium residue and rapid capacity decay encountered in the prelithiation process of ultrathin lithium foils. The doping of Mg and Al significantly improved the mechanical strength of the lithium foils, reducing the risk of fractures in the alloy foils during manufacturing. During the prelithiation process, the extensive microporous structures in the Li-Mg-Al alloy foils facilitated the efficient and smooth transport of lithium ions and electrolytes. This resulted in a threefold increase in the cycle life of the pre-lithiated LFP||graphite full cell. Furthermore, the discharge specific capacity of the LFP was enhanced from 87.8 mAh g^{-1} to 116.3 mAh g^{-1} with prelithiation after 1000 cycles.

Lithium foil contact prelithiation offers simplicity and efficiency, making it suitable for large-scale industrial production. However, the direct contact between the lithium foil and the anode, coupled with the random distribution of contact points, results in heterogeneous lithiation, diversified lithium salts, and an unstable interface. Future research should therefore focus on developing a methode for efficient and uniform contact prelithiation.

3.1.2. Stabilized lithium metal powder (SLMP) prelithiation

Stabilized lithium metal powder (SLMP) is a type of lithium metal in the form of spherical powder with particle sizes ranging from 10-20 μm [87]. SLMP can be stabilized in a dry air atmosphere due to a dense Li_2CO_3 protective layer on the surface of the lithium metal particles, which shields the particles from oxidation by atmospheric oxygen. Jarvis et al. [88] demonstrated that adding 1.93wt% of SLMP to graphite electrodes increased the ICE from 77.9% to 95.4%, confirming that stabilized lithium metal powders serve as excellent additives for lithium replenishment.

SLMP is recognized as an ideal prelithiation material for anode electrodes in LIBs, including Si/C [89] and micrometer-scale SiO/C composite anodes [90] (Fig. 5a). Additionally, SLMP facilitates the formation of intact SEI films when exposed to low external currents. Wang et al. [91] observed that graphite half-cells pre-lithiated with SLMP developed fully functional SEI on graphite after a period of rest. This method of SEI development using SLMP is superior to the slower formation techniques used in conventional LIBs. However, the formation of SEI is inherently slow, and pressure activation is necessary to expedite the process.

The efficiency of dispersing lithium particles into the anode material during lithium replenishment, as well as the compatibility of these particles with the electrolyte, are currently under investigation [92]. Lee et al. [93] proposed a dry prelithiation methode that involves directly adding lithium metal powders onto the surface of Gr/Si electrodes and applying a temperature of 60 °C and a pressure of 550 MPa for lithiation (Fig. 5b). This approach allows fine lithium particles to diffuse uniformly throughout the active material, achieving uniform prelithiation of the electrode. Additionally, the residual lithium particles enhance the lithiation reaction speed of the active material during cycling.

One of the main challenges in the SLMP prelithiation process is to effectively disperse SLMP into the anode material to achieve uniformly dispersed SLMP coatings or composites and to prevent SLMP degradation prior to the coating process. By optimizing the composition of binder solutions, SLMP ensures uniform distribution in the stock for subsequent manufacturing processes. Wang et al. [94] developed a binder system using styrene-butadiene rubber (SBR) and poly (vinylidene fluoride) (PVDF) (Fig. 5c) that can uniformly disperse stabilized lithium-metal powders into the anode electrode material without reacting with SLMP or degrading in conventional NMP solvents, delivering comparable battery performance to conventional PVDF-based electrodes. Jennifer Heine et al. [95] utilized a heptane/polyisobutylene binder suitable for coating lithium powder particles onto electrode materials across a wide temperature range. Ai et al. [96] reported a polymer binder composed of a blend of 0.5 w% polystyrene (PS) and 0.5 w% SBR. When employed with this binder in a xylene solution, it facilitates the extended uniform dispersion of SLMP, which aids in achieving a uniform coating on the surface of the anode material. As depicted in Fig. 5d, after application of this binder solution, the graphite anode surface becomes smoother and flatter, which contributes to the improved decomposition reaction of SLMP during prelithiation. This prelithiation process, when implemented in graphite/NMC full batteries, SiO half-batteries, and SiO/NMC full batteries, results in higher initial cycling efficiencies and enhanced cycling performance compared to configurations without SLMP prelithiation.

SLMP exhibits enhanced stability due to its fine particle size and a

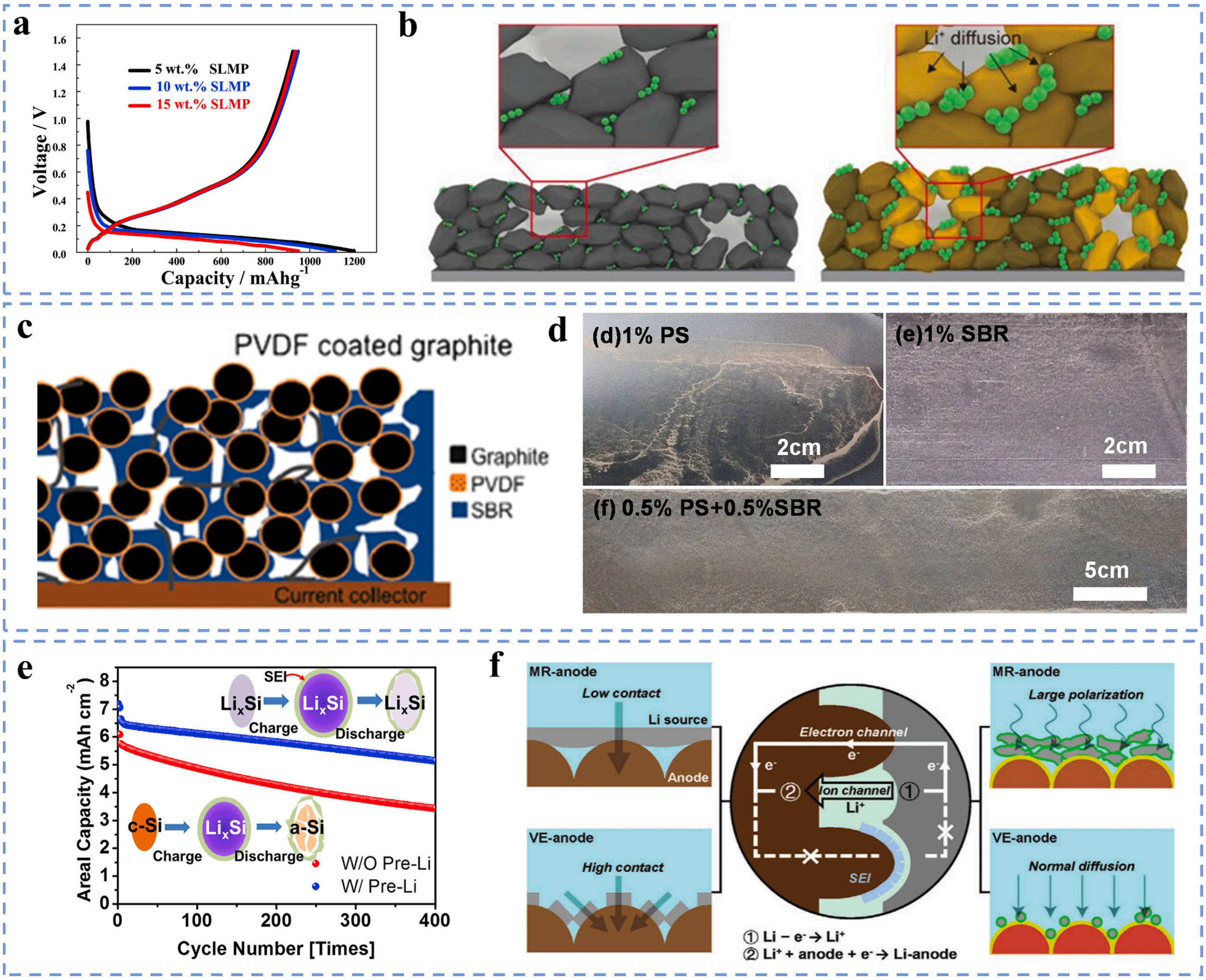


Fig. 5. A) voltage profiles of d-SiO/graphite/carbon prelithiated by varying amount of SLMP [90]. b) Structural and lithiation state changes during each step in the dry prelithiation process [93]. c) Schematic model of PVDF-coated graphite laminated [94]. d) Contrast diagram showing SLMP loading on graphite anode surface using different binder solutions: 1 w% PS, 1 w% SBR, and a combination of 0.5 w% PS with 0.5 w% SBR. [96]. e) Investigation of capacity degradation after 400 cycles in both bare Si-Gr/LiCoO$_2$ (red line) and pre-lithiated Si-Gr/LiCoO$_2$ (blue line) full cells [97]. f) Illustration of the mechanical rolling-guided and vacuum thermal evaporation-guided contact prelithiation from the perspective of anode interface electron channel evolution [98]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protective oxide film on the surface. It can be directly incorporated into the anode material by calculating the required lithium content during the electrode manufacturing stage. Moreover, it promotes a more uniform degree of prelithiation and simplifies the production process, making it a promising methode for commercialization. However, current academic research on the mechanism of SLMP prelithiation is not sufficiently in-depth. According to theoretical calculations, the SLMP added to the electrode does not completely decompose, failing to achieve the initial prelithiation goals. Additionally, due to its high reactivity, SLMP reacts with the electrolyte after being added to the anode, leading to lithium depletion, and thus defeating the purpose of prelithiation. Moreover, the harsh manufacturing process renders SLMP extremely expensive. Consequently, these factors limit the application of SLMP as a prelithiation additive.

3.1.3. *Lithium metal deposition prelithiation*

Controlling the thickness of deposited lithium through physical means, such as evaporation and deposition, has become an effective methode to improve the uniformity of prelithiation. Thermal deposition precisely replenishes the lithium needed for initial battery consumption and fully suppresses the volume expansion of new anode materials, stabilizing the electrode structure. This process, which results in no remaining 'dead lithium' or other by-products, reduces production costs and eliminates the need to disassemble the battery. K.H. Kim et al. [97] controlled the evaporation time to precisely deposit the thickness of lithium, effectively reducing the volume change of the Si-Gr anode during discharge (Fig. 5e). The full cell, composed of a Si-Gr anode and a lithium cobaltate cathode pre-deposited with lithium, demonstrated excellent performance with high-density capacity.

Additionally, Li-M (Sn, Al, etc.) metal composite foils, with their large volume capacity and excellent mechanical properties, are also excellent choices for prelithiation. Zhang et al. [98] introduced a sacrificial ultrathin Li film (<60 μm) onto the anode surface using mechanical rolling (MR) and vacuum thermal evaporation (VE) (Fig. 5f). This method ensures more conformal contact with the abundant electron channels at the interface of the Li film and anode. Consequently, the high mobility rate of the Li vapor allows for better conformal contact with the electron channels, reduces the current density at the contact interface, and improves the stability of the electron channels, which leads to significantly enhanced kinetics in the lithiation process. The prelithiation process guided by VE achieves a lithium utilization of 91.0%.

The lithium deposition method allows precise control of the degree of prelithiation. This is attributed to the enhanced contact area between the active lithium and the anode material, which increases electrical conductivity and allows the lithium source to be fully utilized. It prevents dead lithium from blocking the Li- transport channel and prematurely terminating the prelithiation process. This strategy is crucial for exploring the prelithiation mechanism of advanced battery anodes.

In conclusion, lithium metal contact prelithiation is currently the simplest and most efficient of all pre-lithiation processes. However, there are significant differences in lithium utilization between different prelithiation techniques. The lithium foil contact prelithiation process is characterized by variability in the interfacial contact points of lithium utilization, resulting in relatively low utilization efficiency. Nevertheless, the lithium foil can be reused in subsequent processes after treatment, which, to some extent, improves the efficiency of lithium resources. By calculating the irreversible capacity of the anode prior to consumption, it is possible to achieve efficient utilization of the lithium replenishment agent by accurately controlling the amount of SLMP added during the prelithiation process. Lithium deposition is currently one of the most efficient processes for utilizing lithium resources and achieving the most accurate degree of prelithiation. This process can monitor the thickness of prelithiation in real time using a crystal oscillator, thus obtaining the required thickness of prelithiation on the anode surface.

3.2. *Lithium metal-assisted prelithiation*

The irreversible loss of lithium in the anode can be addressed not only through the self-discharge reaction caused by short circuits, but also indirectly by external field conditions which compensate for the early-stage capacity loss. These methods include electrochemical prelithiation, where a constant current is applied to the electrodes under control of the external circuit of the assembled battery to initiate the electrochemical reaction. Another methode is chemical prelithiation, where lithium is dissolved in a solvent to form a complex, subsequently transferring active lithium to the electrode surface. Additionally, lithium alloy compounds synthesized from lithium metal and anode materials serve as effective anode prelithiation reagents due to their low redox reaction potential and high discharge specific capacity when coated on anode materials.

3.2.1. *Lithium-containing solutions prelithiation*

Lithium-containing solutions prelithiation replenishes the loss of active lithium during the initial cycling process by immersing the anode electrode into a low-potential reducing lithium-containing solution. This method ensures complete infiltration of the lithium-containing solution into the anode pole piece, addressing the issue of uneven lithium distribution encountered with direct lithium metal prelithiation.

Graphite anode electrodes, known for their low ICE due to large irreversible capacity, have been the subject of various studies. M.G. Scott et al. [99] proposed chemically prelithiating graphite electrodes using n-butyllithium to diminish the lithium loss associated with solid electrolyte interphase (SEI) formation. This treatment demonstrated a significant reduction in irreversible capacity. However, the SEIs formed from prolonged n-butyllithium treatment were thicker and more fragile compared to those formed by standard charging and discharging, which could lead to capacity loss due to damage during cycling. Prior research has shown that lithium-containing reagents, such as 1 M lithium biphenyl dissolved in tetrahydrofuran [100–103], can rapidly prelithiate graphite (Fig. 6a, b). Zhang's group [104] reported an SEI layer formation on the anode surface during chemical prelithiation by dissolving lithium biphenyl (Li-Bp) in tetrahydrofuran, which reacts with graphite: $Li^{+} + Bp^{-} + C \rightarrow LiC + Bp$. The ICE of prelithiated hard carbon in a half-cell configuration could be increased to 106 % within 30s post-assembly. The corresponding full cell displayed a substantial improvement in ICE (90.2% vs. 75%) and cycling performance when paired with a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode (Fig. 6c).

To achieve stable prelithiation of graphite-based anodes, Choi et al. [92] developed a Gr/SiO_x composite anode with ideal ICE by chemically lithiating it in a lithium aromatic complex (LAC) solution. This method adjusted the solvation capacity of the solvent without compromising the structural integrity of the electrode. It enhanced the Li anions interactions in weakly solvating solutions and inhibited Li ions desolvation, thus mitigating the embedding of solvated ions in graphite and stabilizing the mixture for prelithiation. The energy density of the prelithiated hybrid anode assembly in full cells was measured to be 506 Wh kg^{-1}, achieving 98.6 % of the theoretical energy density. Jang's group [105] found that while the LAC complex of biphenyl molecules could not add reactive lithium to the SiO_x structure, it did facilitate the formation of a SEI film with the electrolyte, resulting in a modest improvement in ICE. By exploiting the increased lowest unoccupied molecular orbital (LUMO) energy level of a biphenyl molecule derivative, the group lowered the redox potential of the complex to 0.13 V, which is lower than that of SiO_x. This modification actively modulated lithium in SiO_x, achieving an ICE of over 100 %. Consequently, the energy density of the full cell using prelithiated SiO_x anodes was 98.2 Wh kg^{-1} higher than that of the full cell using standard graphite anodes (Fig. 6d, e).

Naphthalene/lithium (Li-Naph) is a commonly used chemical prelithiation reagent due to its spontaneous reaction with anode materials. Shen et al. [106] reported using Li-Naph to prelithiate hard carbon,

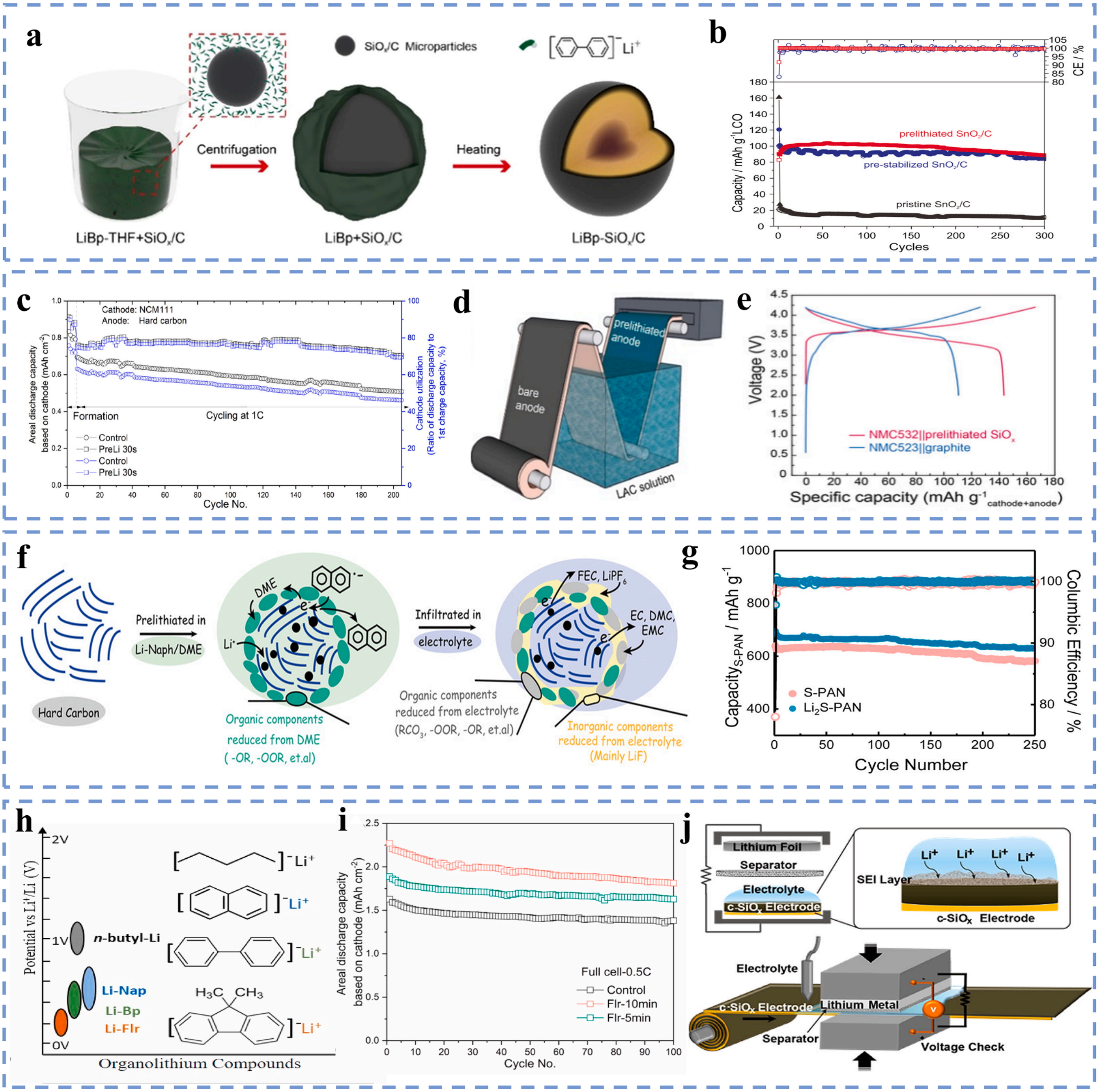


Fig. 6. A) schematic of the synthesis process and reactant microscomic distribution within the solution of libp-sio$_x$/C [101]. b) The cycling performance and CE of LCO||SnO$_2$/C full cells at 1C [102]. c) The cycling performance and CE of LCO||SnO$_2$/C full cells at 1C [104]. d) The cycling performance and CE of LCO||SnO$_2$/C full cells at 1C. [105]. e) The voltage curve of the initial cycle for a NMC532||graphite cell (blue line) versus a NMC532||prelithiated SiO$_x$ cell (pink line) [105]. f) line) [105]. f) The chemical prelithiation process of hard carbon in Li-Naph/DME solution with 2 % FEC [106]. g) [106]. g) The cycling performance and CE of Li$_2$S-PAN and S-PAN electrodes tested over 250 cycles at 100 mA g^{-1} [107]. h) The illustration of the redox potential and molecular formula of Li-Nap, Li-Flr, Li-Bp, and n-butyl-Li low reduction potential prelithiation reagents. [109]. i) The comparison of cycling performance of Flr-5 min, and Flr-10 min and control samples at 0.5C in full-cell format. [109]. j) Illustration of c-SiO$_x$ anode electrochemical prelithiation process in a scalable roll-to-roll process scheme [110]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

creating a pre-generated SEI layer on the electrodes (Fig. 6f). This SEI layer, primarily composed of an organic composite, transforms into a dense and stable inorganic SEI film with LiF as the main component upon initial discharge, effectively compensating for the high irreversible capacity loss. Shen et al. [107] also utilized Li-Naph to fully prelithiate sulfur-polyacrylonitrile (S-PAN) composites for Li$_2$S-PAN anodes and, as a contrast, to partially prelithiate nanosilicon in Li$_x$Si anodes. The Li$_x$Si/Li$_2$S-PAN cells exhibited a higher specific energy of 710 Wh kg^{-1} and an ICE of 93% compared to those of Li$_x$Si cells (Fig. 6g). Ju et al. [108] found that using Li-Naph for prelithiation could result in the degradation of the binder in composite electrodes, leading to decreased battery discharge capacity. Thus, the compatibility of the prelithiation reagent with electrode materials is crucial.

Lithium-containing solutions offer a simple and rapid methode for introducing a lithium source and have an excellent lithiation effect for materials with a high redox potential. However, their lithiation effect is significantly limited for systems with low redox potential, such as silicon and carbon materials. Current prelithiation reagents, such as n-butyllithium, naphthalene, and biphenyl, have high redox potentials and poor prelithiation capabilities. A new organolithium compound has been reported, 9,9-dimethyl-9H-fluorene-tetrahydrofuran (abbreviated as Flr) [109]. The lithiation potential of Flr ranges from 0.02 to 0.4 V (Fig. 6h), providing a lower redox potential advantage. When Flr is used for prelithiating SiO anodes, it forms an SEI layer during prelithiation and preloads a controlled amount of lithium into the SiO electrode. Compared to other prelithiation reagents, Flr achieves a faster prelithiation process at a lower potential of approximately 0.18 V, with a high ICE of around 90.7% in the half-cell after 10 min of prelithiation. A comparative enhancement of the ICE to 87.1% is observed in full cells employing a $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode when paired with prelithiated SiO/G anodes, in contrast to a 61.1% ICE without prelithiation (Fig. 6i).

Prelithiation using lithium-containing solutions effectively regulates prelithiation levels in electrodes by managing the duration to achieve uniform prelithiation. However, this strategy requires the selection of prelithiation reagents with sufficiently low redox potentials (<0.2 V) and places high demands on the choice of solvent and intermediate organic matter.

3.2.2. Electrochemical prelithiation

Electrochemical prelithiation, which involves applying a constant current to an electrolytic cell to initiate an electrochemical reaction, replenishes the lithium loss from the anode material. This method is used to compensate for the irreversible capacity losses caused by the formation of a SEI film and the occurrence of side reactions. By optimizing the circuit resistance and monitoring the voltage between the two electrodes, the prelithiation process is precisely controlled. The degree of prelithiation is regulated by adjusting the duration of the discharge process and the cut-off potential. Typically, the electrochemical prelithiation process is carried out at low current densities to achieve precise control. Moreover, it requires a tightly controlled voltage range to prevent lithium plating and other side reactions. This process is typically conducted in a laboratory stage using an assembled half-cell, similar to the anodic contact prelithiation process. However, the cells must be disassembled and reassembled after prelithiation, rendering it unsuitable for large-scale industrial production.

Kim et al. [110] fine-tuned the degree of prelithiation of the SiO_x anode by using precise short-circuit timing and voltage monitoring. They adjusted the lowest potential to a point below the SEI layer formation, which prevents electrolyte decomposition, yet above the main alloying reaction point. The electrochemical reaction at the electrode can be controlled by modulating the potential change. After optimizing the circuit, prelithiation of the original electrode by short-circuiting with Li foil (Fig. 6j) resulted in CE levels of 94.9%, 95.7%, and 97.2% in the first three cycles. Arlavinda Rezqitaz constructed half-cells by assembling Si/C anode electrodes with lithium foils and pre-lithiating them at 0.1 V and 0.5 V [111]. The pre-lithiated Si/C electrodes were then disassembled and assembled into NMC532||Si/C full cells to investigate the impact of prelithiation on the electrochemical performance of the full cell at different voltages. There was no lithium deposition on the lithiated Si/C at 0.5 V, attributed to an uncompleted reaction under a high reaction potential for the lithiation process. The electrode continued to lithiate in the subsequent full cell, resulting in a reduction of the stabilized capacity for the full cell. Lithium was deposited on the lithiated silicon/carbon anode at 0.1 V (relative to Li/Li^+). After full lithiation and stabilization of full cell performance, a higher capacity was achieved.

Electrochemical prelithiation enables precise control of the oxidation potential required for prelithiation using external circuitry, forming the SEI film, enhancing electrochemical properties, and preventing lithium deposition caused by transition lithiation. Strict control of the degree of prelithiation is crucial during the prelithiation process. If the potential of the anode falls below or equals the equilibrium potential of Li^+/Li, lithium plating may occur, leading to safety issues. Furthermore, excess lithium can obstruct the diffusion channels of lithium ions, ultimately reducing the CE of the full cell. This prelithiation strategy can be fully integrated into existing roll-to-roll production processes. Anode material pre-lithiated electrochemically can continue to react in air if it has not reached the equilibrium transition state. Therefore, it is necessary to protect the pre-lithiated electrode in an inert atmosphere, increasing the complexity of the subsequent process and raising the cost of battery manufacturing.

3.2.3. Lithium alloy compounds prelithiation

Lithium alloy compounds, such as Li_xSi, Li_xSn, and Li_xGe, are considered potential replacements for the next generation of anode materials due to their high capacity and lithium content. However, these compounds tend to be chemically reactive and possess low redox reaction potentials, which render them unstable in air. Therefore, enhancing their chemical stability is essential for their utilization as prelithiation additives. A series of electrode materials have been screened based on the de-embedded lithium potential of the anode material and the electrochemical window of the electrolyte to ensure stable operation over a wide potential range. Interfacial modifications, including capping, doping, and coating, are employed to stabilize the electrode surface and expand the applicable potential range. These modifications also contribute to the formation of a more stable SEI film, which prevents lithium depletion from the cathode.

Typical modifications for Li_xZ (where Z = Si, Ge, Sn, etc.) alloys involve coating their surfaces with layers of inert lithium-containing compounds, such as Li_2O and LiF. This coating isolates the lithium alloys from external air and moisture, thereby maintaining the stability of the material. Zhao et al. [112] synthesized $Li_{22}Z_5$ alloys and $Li_{22}Z_5$–Li_2O composites (Fig. 7a) using a one-step metallurgical process. This approach improved the ICE of graphite and alloy-based anode materials. Both the $Li_{22}Z_5$ alloy and the $Li_{22}Z_5$-Li_2O composites exhibit high capacity and low chemical potentials due to their inherent chemical reactivity. Prelithiation with these materials emerges as a promising strategy for enhancing anode performance. Among all Group IV alloys, LixGe shows superior stability under ambient air conditions once lithiated. The lithiation of ZO_2 produces composites with uniformly dispersed reactive Li_xZ nanodomains within a robust Li_2O matrix, effectively preventing oxidation. The strong bond between oxygen atoms in Li_2O and lithium atoms in $Li_{22}Z_5$ stabilizes the reactive $Li_{22}Z_5$ nanodomains, leading to increased ambient air stability in $Li_{22}Z_5$-Li_2O composites.

Li_xSi alloys are currently the most extensively studied lithium alloy compounds due to their straightforward synthesis process and the broad availability of raw materials. Zhao et al. [113] examined Li_xSi-Li_2O core–shell nanoparticles as a prelithiation reagent (Fig. 7b). These nanoparticles, processed in a slurry, exhibit high capacity in dry air conditions, protected by Li_2O passivation shells. When introduced into the electrolyte, Li_xSi- Li_2O can directly pre-lithiate silicon and graphite anodes. However, the formation of the Li_2O passivation layer consumes some active lithium, resulting in a prelithiation capacity of only 1310 mAh g^{-1} for Li_xSi-Li_2O. To address this issue, Zhao's group [114] synthesized Li_xSi nanoparticles via thermal alloying (Fig. 7c) to serve as a high capacity prelithiation reagent that enhances stability. By reducing 1-fluorodecane on the surface of Li_xSi through surface modification, they created a continuous and dense coating resembling an SEI. This coating, primarily composed of LiF and alkyl lithium carbonate with long hydrophobic carbon chains, effectively reduces side reactions under ambient conditions. The coated Li_xSi nanoparticles exhibit a high capacity of 1600 mAh g^{-1} in dry air conditions at 10% relative humidity. However, both coatings are incompatible with current slurry processing methods that involve PVDF and CMC-SBR. Identifying a compound compatible with existing battery production processes is crucial. The researchers found that Li_xSi@LiF is compatible with slurry processing using anhydrous N-methyl-2-pyrrolidone (NMP) solvents, providing a high prelithiation capacity of 2504 mAh g^{-1} [115]. It demonstrates exceptional stability in humid air (approximately 40 % RH),

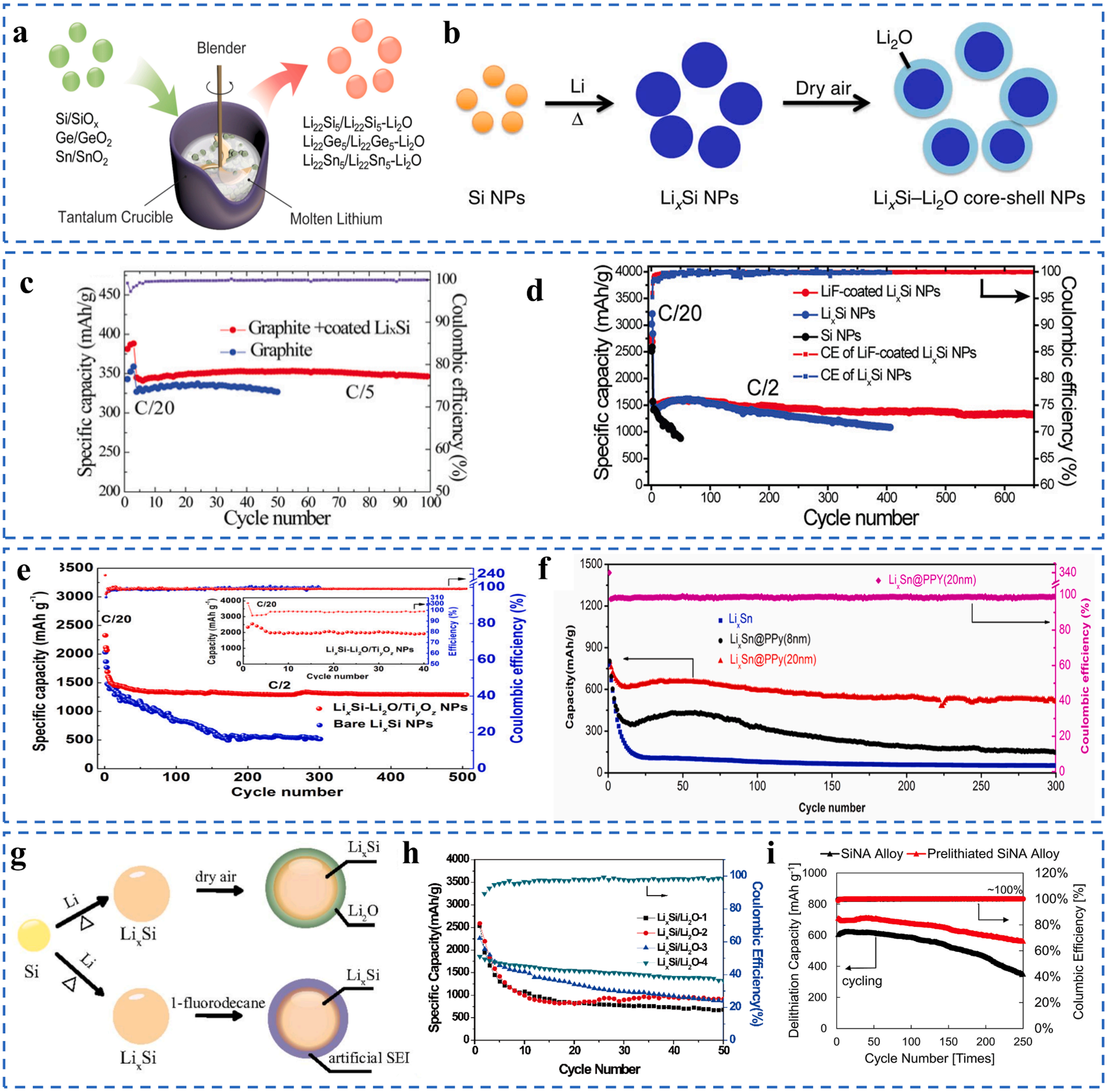


Fig. 7. A) schematic diagram showing the synthesis of $li_{22}Z_5$ alloy and $Li_{22}Z_5$-Li_2O composites using one-pot metallurgical process with molten lithium and Z/ZO_2 (Z = Si, Ge and Sn) as starting materials [112]. b) The diagram of which reacted molten Lithium with Li_xSi NPs under dry air to form Li_xSi-Li_2O core–shell NPs [113]. c) Cycling performance testing was conducted on graphite/coated Li_xSi composite anode and graphite control anode at 0.05 C for the initial three cycles and 0.2 C for subsequent cycles [114]. d) The cycling performance of LiF-coated Li_xSi nanoparticles, Si nanoparticles control cell, and bare Li_xSi nanoparticles was evaluated at 0.02 C for the initial cycles and 0.5 C for subsequent cycles [115]. e) Cycling performances of bare Li_xSi nanoparticles and Li_xSi–Li_2O/Ti_yO_z core–shell nanoparticles were assessed under varying current densities: 0.02 C for the initial three cycles and 0.5 C for the subsequent 500 cycles within the voltage range of 0.01–1 V [116]. f) The cycling performances of Li_xSn anode and Li_xSn@PPy anodes with different coating thickness [117]. g) Two approaches to stabilize reactive Li_xSi NPs [118]. h) The cycling performance of four groups Li_xSi/Li_2O samples at 0.02 C [120]. i) Delithiation cycling capacity and columbic Efficiency of SiNA and prelithiated SiNAover 250 cycles at 0.5 C [121].

maintaining 85.9 % capacity retention after 24 h due to the low solubility of LiF in water, as shown in Fig. 7d.

Beyond the more common coatings such as Li_2O, LiF, and artificial SEI coatings, other types of coatings and functions have been developed to address the issues of structural defects and poor electrical conductivity associated with Li_2O and LiF coatings. Wang et al. [116] devised a simple lithiation method to fabricate lithiated TiO_2-protected Li_xSi nanoparticles (Li_xSi-Li_2O/Ti_yO_z NPs) as anode materials. This dense TiO_2 coating shields the internal Li_xSi alloys from environmental corrosion, resulting in enhanced stability under dry air conditions. In a half-cell configuration with a Li_xSi-Li_2O/Ti_yO_z anode electrode, a capacity of 1300 mAh g^{-1} was retained after 500 cycles at 0.5C (Fig. 7e), achieving a capacity retention of 77%. Li et al. [117] applied a layer of conductive polypyrrole to coat the surface of tin nanoparticles. This coating remained structurally intact during lithiation, ensuring that the Li_xSn nanoparticles maintained high stability under dry air conditions. The flexible and conductive polypyrrole also accommodates the significant volume changes of the Li_xSn nanoparticles and enhances interparticle electronic connectivity. They reported that the Li_xSn@PPy (20 nm) composite maintained a stable reversible capacity of 534 mAh g^{-1} after 300 cycles (Fig. 7f), even after exposure to dry air for 5 days. Additionally, the prelithiation capacity of the composite remained above 75 %.

When lithium alloy compounds are directly or indirectly used as anode materials, challenges such as volume expansion, strong chemical reactivity, and other material properties limit their development as prelithiation reagents. The electrochemical properties of Li_xSi nanomaterials often depend on the material type and particle size. Thus, enhancing these properties through structural design or additive modification is necessary. Zhao et al. [118] prepared Li_xSi/Li_2O composites using inexpensive SiO or SiO_2 (Fig. 7g). The resulting composites, composed of homogeneously dispersed Li_xSi nanodomains embedded in a highly crystalline Li_2O matrix, provide exceptional stability. These composites can be easily integrated with various anode materials to achieve high ICE greater than 100%. Li's group [119] conducted a systematic investigation of Li_xSi alloy compounds with nitride protection. They found that the cycling performance improved as the nitride layer ($Li_xN_ySi_z$) formed on the surface of Li_xSi, maintaining a capacity of over 1200 mAh g^{-1} after 80 cycles. As the degree of nitriding increased, the capacity retention notably improved from an average decay rate of 1.06% to 0.15% per cycle. However, due to silicon inactivation within the $Li_xN_ySi_z$ layer, the initial discharge capacity was reduced. Han et al. [120] examined the performance of SiO_2 particles of varying sizes (6 nm, 20 nm, 300 nm, and 3 μm) on Li_xSi/Li_2O composite anode materials. The lithiated product from micron-sized SiO_2 particles demonstrated superior performance, exhibiting an initial charging capacity of 1859 mAh g^{-1} and maintaining above 1300 mAh g^{-1} after 50 cycles (Fig. 7h). Pankaj K et al. [121] synthesized a pre-lithiated silicon nano-alloy material through mechanical milling and pyrolysis of hard lithium tallowate and Si nanoparticles. Prelithiation enables the material to compensate for initial irreversible losses caused by the decomposition of lithium compounds. This process forms protective artificial SEI and prefills the mechanically cracked voids of the silicon nano-alloys (SiNAs), improving long-term manufacturability and the mechanical properties required for cyclability. The pre-lithiated SiNAs exhibit a high Coulomb cycling efficiency of 90% as shown in Fig. 7i.

Lithium alloy compound additives demonstrate a substantial prelithiation capacity, effectively compensating for the initial irreversible capacity of anode electrodes with only minor additions. However, their increased chemical reactivity introduces significant safety concerns and makes them unsuitable for current slurry-based electrode preparation methods that use NMP or water as solvents, thereby restricting their practical applications. This overview of anode prelithiation offers valuable insights for advancing post-LIBs technologies and may encourage further research into anode prelithiation reagents.

4. Cathode-assisted prelithiation strategy

During the initial discharge of LIBs, the formation of the SEI and irreversible loss of active material led to a reduced reversible capacity in subsequent cycles. Typically, the graphite anode experiences an irreversible capacity loss of between 7% and 20%, the silicon/carbon nanoparticle anode about 30%, and the transition metal oxide anode around 50%. Efficient lithium replenishment using anode additives is an effective method, in addition to active lithium replenishment directly on the anode material [122,123]. Cathode prelithiation additives must compensate for this irreversible capacity loss with a small quantity of additive, necessitating a high theoretical capacity. Potential cathode prelithiation additives are typically selected from materials with lithiation potentials above the minimum anode discharge potential and delithiation potentials below the maximum anode charging potential. This selection ensures that the additive reacts early and achieves lithium replenishment before the anode reaches its lithiation potential. A suitable prelithiation additive for the cathode should be compatible with the original manufacturing process without introducing additional processes or compromising the structure and performance of the battery.

4.1. Lithium-rich cathode materials

Lithium-rich cathode materials, such as Li_2MnO_3, $LiNiMnO_4$, and $LiVPO_4F$, can store more Li ions by leveraging the properties of their own structure. This method of prelithiation is promising as it does not generate excess by-products after lithiation. After releasing its stored lithium ions, a lithium-rich cathode material cannot undergo a reversible reaction due to the high oxidation potential of its lithiation reaction. This characteristic provides an additional source of lithium to compensate for the initial irreversible capacity loss of the negative electrode.

The Li-rich and Mn-rich layered oxide cathode material Li_xMnO_y was found to exhibit a specific capacity greater than 250 mAh g^{-1} at voltages higher than 4.5 V in the initial cycle [124], making it a promising candidate for advanced cathode materials. The oxides in this class possess unique octahedral and tetrahedral central sites that can reversibly embed Li^+ through the Mn^{3+}/Mn^{4+} conversion (Fig. 8a). The prelithiated layered Li_2MnO_3 is more thermodynamically stable and can provide an excess of lithium ions to replenish the anode electrode's initial-cycle irreversible capacity. D. Peramunag [125] discovered that the spinel $Li_xMn_2O_4$ (where $x = 0.2, 0.3, 0.4, 0.6$, and 1.0), which was prelithiated using n-butyllithium and formed by cubic spinel $LiMn_2O_4$, was fully utilizable during charging with chemically introduced Li^+ at a low voltage plateau (3 V). Tarascon et al. [126] reported the effective utilization of the octahedral void through chemical prelithiation, although issues such as low utilization of stored Li and less than 3% change in volume of Li^+ during insertion into the octahedron have been noted. This can lead to a phase transition of the electrode during cycling, resulting in the destruction of the electrode structure and loss of battery capacity.

Layered Li_xMnO_y cathode materials have a higher specific capacity than conventional cathode materials, but they suffer from rapid capacity decay, poor multiplicity performance, and a rapid voltage drop during cycling. Research has shown that doping Li_xMnO_y with elements such as Ni, Mg, Co, and Al can enhance its cycling stability and multiplicity performance [127–129]. Modified $LiNiMnO_4$ materials are the most commonly used lithium-rich materials, owing to their simple fabrication process that does not require expensive lithium reagents or lithium metal (Fig. 8b). However, the manufacturing of existing $LiNiMnO_4$ lithium-rich cathode materials is costly. Therefore, finding a simple and cost-effective method for material preparation is crucial. Aravindan [130] used Ni-doped spinel $LiNi_{0.5}Mn_{1.5}O_4$ for primary lithium storage at a low voltage plateau of 2.8 V. Subsequent cycles involved repeated lithium depletion at a voltage plateau of 3.5–5 V (Fig. 8c), using the tetrahedral reversible intercalation sites with the desired amount of lithium (0.33 mol). The $LiNi_{0.5}Mn_{1.5}O_4$ fibers were pre-lithiated to the octahedral sites with 0.33 mol, avoiding the effects from the tetrahedral sites and depletion of lithium from the tetrahedral sites of $LiNi_{0.5}Mn_{1.5}O_4$. This approach has been experimentally proven to be feasible.

Rosenberg et al. [131] introduced Li^+ into the 16c octahedral sites of the $Li_{1.05}Ni_{0.05}Mn_{1.9}O_4$ (4 V) and $LiMn_{1.5}Ni_{0.5}O_4$ (5 V) spinel host structures (Fig. 8e) using activated spinel materials, $LiOH\text{-}H_2O$ (99%) and tetraethylene glycol (TEG). These materials reacted fully under microwave activation, and the process did not require an inert atmosphere or humidity control, making it compatible with existing battery manufacturing processes. Wesley M. Dose's group [132] proposed a method for lithiating spinel materials by dissolving lithium metal in liquid ammonia, conducted at 5 V using Si-graphite anode electrodes. A

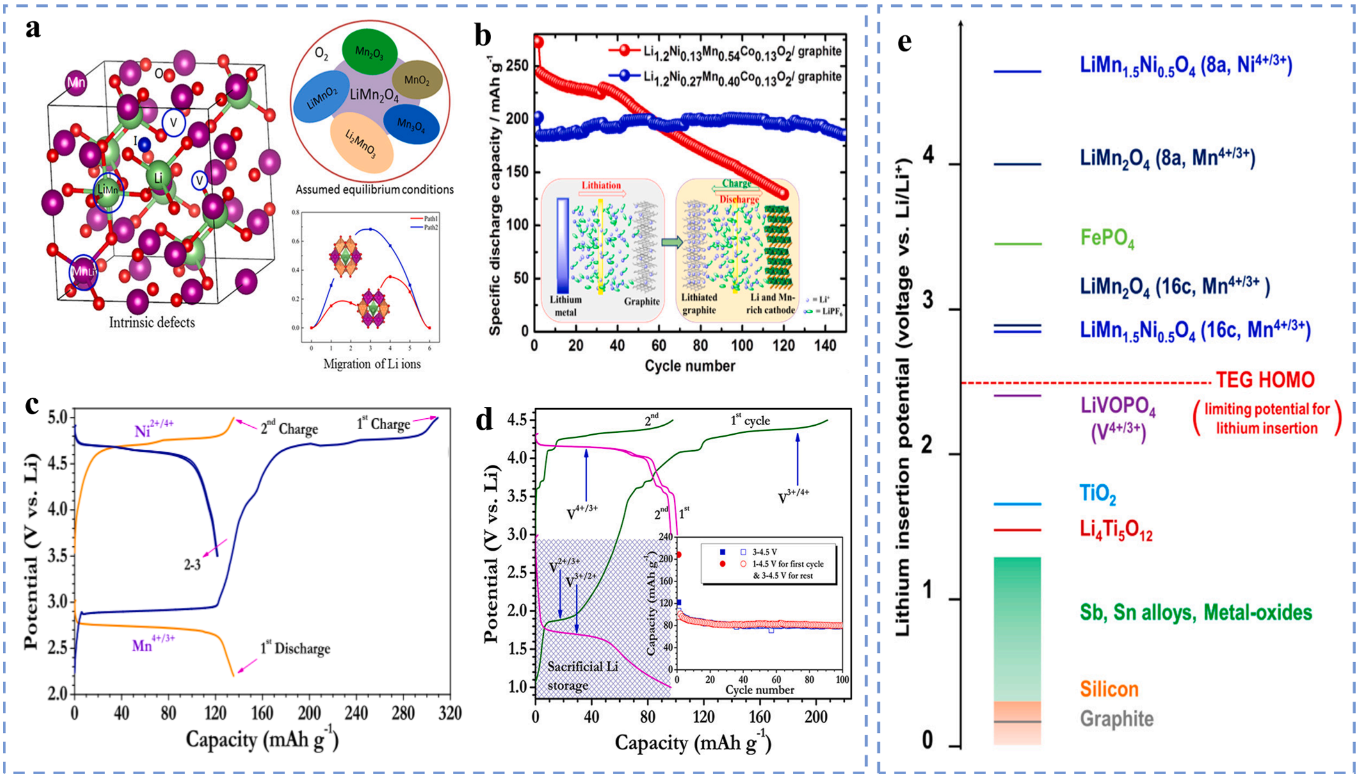


Fig. 8. a) Intrinsic point defects in spinel $LiMn_2O_4$ and diffusion barriers around $LiMn_2O_4$ defects for Li-ions [124]. b) Cycle performance comparison of $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$||graphite and $Li_{1.2}Ni_{0.27}Mn_{0.40}Co_{0.13}O_2$ ||graphite full cells at 30 °C [128]. c) Two charging and discharging plateaus of $LiNi_{0.5}Mn_{1.5}O_4$ cathode in a half-cell for the first and second cycles [130]. d) Two charging and discharging plateaus of tavorite-type $LiVPO_4F$ cathode in a half-cell for the first and second cycles, with the inset showing the corresponding cycling performance of tavorite-type $LiVPO_4F$ [133]. e) Comparison of the potential for lithium insertion to the highest occupied molecular orbital of TEG with the voltage of the Li/Li^+ couple [131].

full cell, comprising a silicon-graphite anode and a lithiated $Li_{1+x}Ni_{0.8}Co_{0.2}O_2$ ($x = 0.62$) cathode, demonstrated a reversible capacity 23% higher than the ICE of the un-lithiated $LiNi_{0.5}Co_{1.5}O_2$ electrode. However, this over-lithiation process is sensitive to air and moisture. To ensure the reaction proceeds smoothly, it is necessary to maintain low temperatures, achievable by adding dry ice. Despite its effectiveness, this method is not suitable for large-scale practical applications due to its sensitivity to environmental conditions.

The $LiVPO_4F$/α-Fe_2O_3 nanofibre cathode material, similar to $LiMn_{1.5}Ni_{0.5}O_4$, can also incorporate extra lithium ions into the cathode through the $V^{3+}/^{2+}$ oxidation–reduction couples at 1.7 V [133]. Additional lithium ions are subsequently released to compensate for the initial capacity loss using the $V^{3+}/^{4+}$ reaction at 3–4 V (Fig. 8d). Unlike the spinel $Li_{1+x}Mn_2O_4$ cathode, $Li_{1+x}VPO_4F$ exhibits a lower redox potential (1.7 V vs. Li/Li^+) and is unstable, showing significant volume expansion during the $V^{3+}/^{2+}$ redox reaction. Thus, the Li embedding/de-embedding process is limited to the first cycle. All the methods listed above are effectively used for alloyed and converted anodes to prevent the irreversible depletion of lithium ions during the first cycle.

Lithium-rich cathode material serves as a simple and efficient method to enhance battery capacity, compatible with the existing battery production process and eliminating the need for additional processes. However, there is disagreement regarding the charging and discharging mechanisms at the two voltage plateaus during the initial cycle [134,135]. Furthermore, the oxygen redox reaction in lithium-rich cathode materials enhances capacity but also leads to irreversible oxygen loss. The prelithiation process poses challenges such as reduced capacity for lithium replenishment, a limited range of material selection, and increased manufacturing costs.

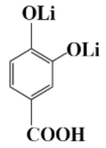
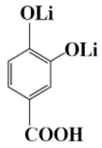
4.2. *"Sacrificial salt" lithium-rich compounds additives*

"Sacrificial salts" such as azides, lithium oxides, lithium organic compounds, and lithium carbonate, contain a large number of lithium atoms within oxidizable anions. These anions lose electrons during the first charge to form Li^+ donors and gaseous substances (e.g., CO, CO_2, or N_2) [122,123,136], as shown in Table 2 and Fig. 9a. These lithium ions can be used to compensate for the lithium lost during the first cycle, thereby increasing the energy density of batteries.

4.2.1. *Inorganic lithium-rich compounds*

Li_2O, Li_2O_2 and Li_2CO_3 are among the most common lithium compounds with high theoretical specific capacities and are frequently investigated as prelithiation additives. Diaz-Lopez et al. [138] synthesized Li_2O:$Li_{2/3}Mn_{1/3}O_{5/6}$ nanocomposites using conventional cathode additives. These nanocomposites displayed a high irreversible capacity of up to 1,157 mAh g^{-1}, augmented by the reaction between Li_2O and $Li_{2/3}Mn_{1/3}O_{5/6}$. During the initial charging period, electrochemically active Li_2O serves as a Li^+ donor. The addition of a nano-sized composite of only 2 wt% Li_2O to the cathode mixture resulted in a 13% increase in the first charge capacity of $LiFePO_4$ and $LiCoO_2$ (Fig. 9b, c). The smaller amount of gas released during the decomposition of the composite, compared to that from the sacrificial salt, reduces the potentially harmful effects of gas precipitation on the electrodes during battery cycling. Bie et al. [139] utilized Li_2O_2 as a cathode additive to compensate for first-cycle lithium loss in LIBs. They found that ball-milled NCM-6 h/Li_2O_2 (Fig. 9d) effectively catalyzed the complete decomposition of Li_2O_2 within a certain range of operating voltages. This resulted in the irreversible compensation of Li^+ and minimal release of O_2, leaving no residue. Any released O_2 can be removed after battery fabrication during industrial production. Li_2O_2 can be prepared

Table 2
Cathode "sacrifice salt" decomposition equation.

Materials	reaction equation	Decomposition Voltage	Ref.
Li_2O	$Li_2O \rightarrow 2Li^+ + 1/2O_2\uparrow + 2e^-$	4.5 V	[138]
Li_2O_2	$Li_2O_2 \rightarrow 2Li^+ + O_2\uparrow + 2e$-	4.3 V	[139]
Li_2CO_3	$Li_2CO_3 \rightarrow CO_2 + 1/2O_2\uparrow + 2Li^+ + 2e^-$	4.75 V	[140,141]
Li_3N	$Li_3N \rightarrow 3Li^+ + 1/2N_2\uparrow$	4.1 V	[142,143]
Li_2S	$Li_2S \rightarrow 2Li^+ + S + 2e^-$	<3.5 V	[144,145]
$Li_2C_2O_4$	$Li_2C_2O_4 \rightarrow 2Li^+ + CO_2\uparrow$	>4.7 V	[146,147]
$Li_2C_4O_4$	$Li_2C_4O_4 \rightarrow 4CO\uparrow + 2Li^+ + 2e^-$	>4.0 V	[44]
	 $+ 2Li^+ + 2e^-$	3.25 V	[148]
Li_2NiO_2	$2Li_2NiO_2 \rightarrow 2NiO + 4Li^+ + 4e^- + O_2\uparrow$	3.5 V	[150]
Li_5FeO_4	$Li_5FeO_4 \rightarrow Li_3FeO_{3.5} + 0.25O_2\uparrow + 2Li^+ + 2e^-$	3.5 V	[151]
	$Li_3FeO_{3.5} \rightarrow LiFeO_2 + 0.75O_2\uparrow + 2Li^+ + 2e^-$	4.0 V	
Li_2CuO_2	$Li_2CuO_2 \rightarrow LiCuO_2 + Li^+ + e^-$ $2LiCuO_2 \rightarrow 2Li^+ + 2CuO + O_2\uparrow + 2e^-$	>3.5 V	[152]
Li_6CoO_4	–	3.4 V	[153]
Li_2MoO_3	–	<3.4 V	[149]

using conventional solvents and binders due to its excellent chemical stability at room temperature, which makes it a promising additive for anode prelithiation.

Pure Li_2CO_3 as a cathode active material exhibits an obvious charging plateau that can reach up to approximately 4.75 V (vs. Li/Li^+) [140]. However, this voltage is well beyond the upper limit of the charging voltage for practical batteries, which limits the application of Li_2CO_3 as a cathode additive. Zhu et al. [141] utilized defective transition metal-doped lattice engineering to obtain Co-Li_2CO_3@LCO materials. The successfully embedded lithium plateau and overpotential were reduced to 4.25 V and 4.4 V (vs. Li^+/Li), aligning with the actual operating voltage of LIBs. In an NCM-811||SiO/C full cell containing 9 wt% Co-Li_2CO_3@LCO cathode additives, there was an initial discharge capacity increase from 196.1 mAh g^{-1} to 229.6 mAh g^{-1}.

Li_3N and Li_2S in lithium-rich compounds exhibit much higher theoretical specific capacities than other compounds. These compounds can increase the theoretical capacity of cathode materials by more than tenfold, and only a small amount of these compounds is needed to satisfy the demand for prelithiation. Commercial Li_3N exhibits a high open circuit voltage (1.16 V vs. Li^+/Li) and a capacity of 1761 mAh g^{-1}. Li_3N powder can be processed via slurry coating for electrode fabrication using low-polarity solvents. Sun et al. [142] synthesized Li_3N through the reaction of metallic lithium with nitrogen. Subsequent annealing produced a dense surface passivation layer comprising crystalline Li_2O and Li_2CO_3, which effectively protected the active components of the material from exposure to ambient air, thereby ensuring the stability of Li_3N particles under ambient conditions. With a 2.5% Li_3N additive, the $LiCoO_2$ electrode provided a 51 mAh g^{-1} higher capacity than the pristine $LiCoO_2$ electrode (Fig. 9e) and showed stable cycling performance. Kyusung Park et al. [143] developed a new electrode structure containing Li_3N that enables reversible Li^+ insertion in alloys and compounds during fast charging. The Li_3N-coated $LiCoO_2$ electrode demonstrated high reversible capacity without any loss of multiplier performance in a full cell with a high-capacity Si composite anode (Fig. 9f).

Li_2S exhibits a high theoretical specific capacity of 1166 mAh g^{-1}, making it a promising candidate as an anode prelithiation reagent [144]. Zhan et al. [145] designed core–shell Li_2S/KB/PVP nanocomposites by mixing Li_2S, KB, and PVP in anhydrous ethanol (Fig. 9g). The active lithium within this core–shell structured Li_2S/KB/PVP material can fully compensate for the loss of active lithium resulting from the formation of an SEI on the surface of Si-C anode electrodes. In a $LiFePO_4$/(Li_2S)/graphite full cell, there was a surplus of 25 mAh g^{-1} higher initial specific charging capacity compared to a $LiFePO_4$/graphite full cell at 0.5C. The initial specific charging capacity for the full cell amounted to 174.4 mAh g^{-1}, with additional capacity stemming from the decomposition of Li_2S.

4.2.2. Organic lithium-containing compounds

Organic lithium compounds are extensively utilized as additives due to their beneficial environmental properties. Lithium oxalate markedly compensates for the lithium lost during the initial cycle. The CO_2 released during the oxidation process is believed to enhance the interfacial stability of graphite and lithium metal anodes and to reduce electrolyte loss. Sophie et al. [146] demonstrated that adding 2.5 wt% and 5wt% lithium oxalate to cathode electrodes increased the first cycle charging capacity by approximately 10% and 20%, respectively, without compromising the electrochemical performance in subsequent cycles. Additionally, the CO_2 release during the oxidation of lithium oxalate prevents the formation of soluble lithium alcohol salts and subsequent transesterification reactions within the electrolyte. Moreover, the reduction of CO_2 may lead to the reformation of lithium oxalate at the anode. This compound dissolves in the electrolyte and is reoxidized at the cathode, generating shuttle currents. The CO_2/oxalate shuttle mechanism thus contributes to the charging capacity without impacting the discharge capacity. Therefore, lithium oxalate acts as a sacrificial salt to replace lost active lithium, while the generated CO_2 enhances the electrode's conductivity and prevents side reactions. However, the commercial application of lithium oxalate is constrained by its high delithiation potential, which exceeds 4.7 V. Research into suitable catalysts to reduce this potential is necessary. Huang et al. [147] developed a new double-layer electrode by optimizing the types of conductive additives and incorporating nanostructured catalysts such as NiO and MnO_2. They successfully lowered the delithiation potential of $Li_2C_2O_4$ from 4.778 V to 4.288 V. Applied to prelithiation of hard carbon anodes, $Li_2C_2O_4$ effectively increased the first cycle capacity of the battery from 79.0 mAh g^{-1} to 140.0 mAh g^{-1}. Furthermore, Wang's group [148] synthesized the organic prelithiation additive Li_2DHBA through a straightforward chemical reaction between LiH and 3,4-dihydroxybenzoic acid. During charging, Li_2DHBA showed a significant specific capacity of 318.9 mAh g^{-1} at voltages ranging from 2.0 to 4.3 V, whereas its discharge-specific capacity was only 17.3 mAh g^{-1}. These results underscore the efficacy of Li_2DHBA as a prelithiation additive (Fig. 9h), highlighting its potential due to high prelithiation capacity, cost-effectiveness, and safety.

4.2.3. Li_xMO_y (M = Fe, Co, Ni, Cu and Mo) series of lithium-rich transition metal oxides

The Li_xMO_y series, featuring transition metals such as Fe, Co, Ni, Cu, and Mo, has been extensively studied as cathode prelithiation reagents. These materials demonstrate high initial irreversible capacity ratios, rendering them unsuitable as cathode materials but ideal as cathode prelithiation additives.

Li_2MoO_3, which is both chemically and structurally stable at room temperature, serves as a cathode additive with a theoretical discharge capacity of 339.6 mAh g^{-1} and a charge capacity of 232 mAh g^{-1}. It features a sloped discharge voltage profile beginning at 3.4 V, which can be utilized to modulate the charging and discharging characteristics of LIBs. Park et al. [149] enhanced the $LiCoO_2$ cathode by incorporating a solid solution of 9 wt% $LiFeO_2$ and 1 wt% Li_2MoO_3. This additive stabilized $LiCoO_2$'s crystal structure and reduced molybdenum dissolution during charging, thus mitigating the instability of LIBs at elevated temperatures. The enhanced battery composition maintained an 85.3% capacity retention rate after 100 cycles within a voltage range of 0–4.3 V (Fig. 10a). However, the practical application of Li_2MoO_3 is limited by

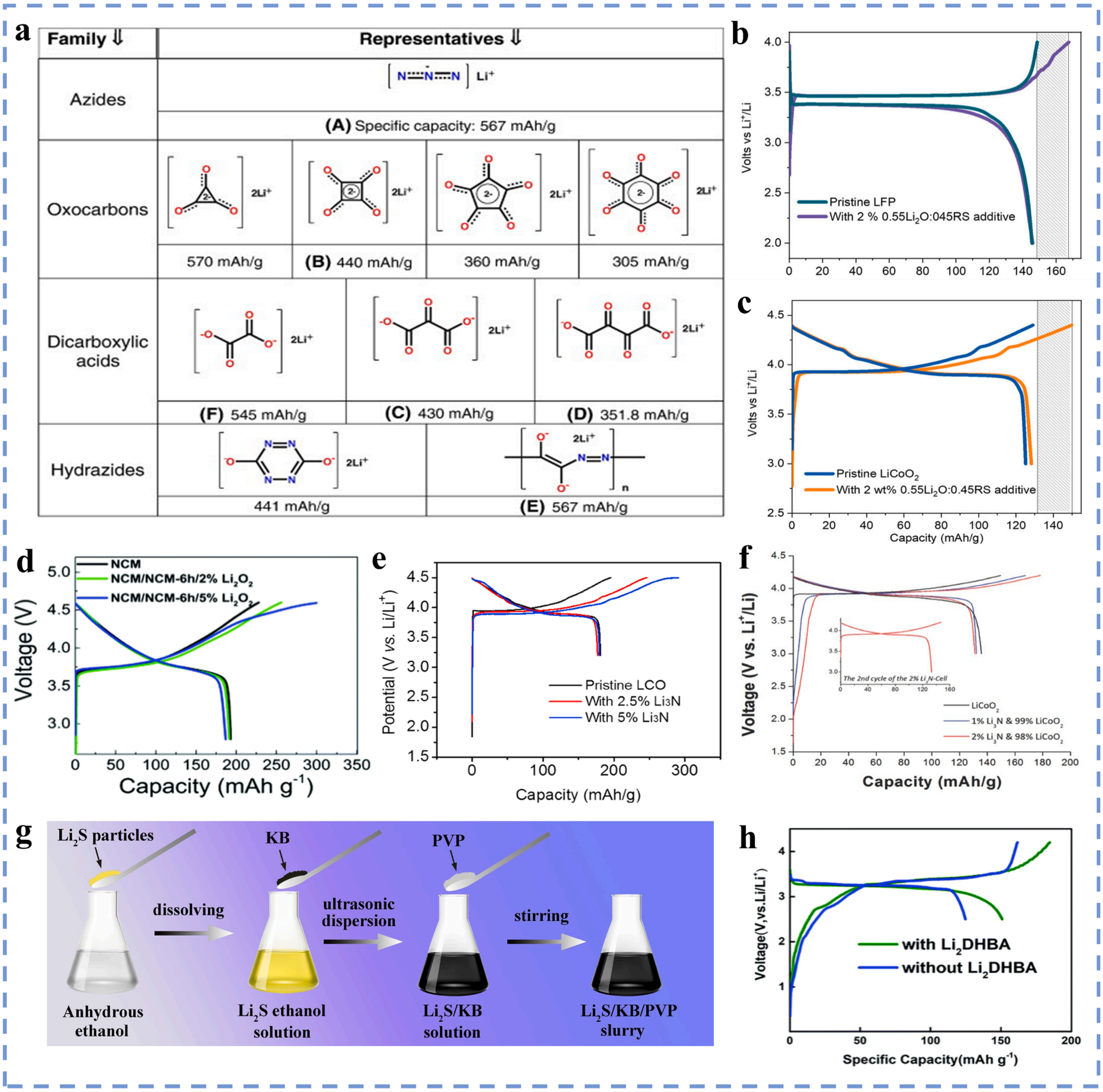


Fig. 9. a) Structural formulae of the compounds corresponding to the various families of 'sacrificial salts'. [137] b) the first charge and discharge performance of LFP with 2 wt%. and c) $LiCoO_2$ with equal addition [138]. d) The charge/discharge curves of NCM electrodes with 2 wt% and 5 wt% Li_2O_2 additives [139]. e) The initial charge and discharge curves of $LiCoO_2$ cathodes with and without the addition of Li_3N [142]. f) The initial charge/discharge voltage curves of $LiCoO_2$ were measured between 3.0 and 4.2 V at 0.1 C for the blend electrodes [143]. g) Schematic of Li_2S/KB/PVP core–shell material synthesized by simple dissolution in anhydrous ethanol [145]. h) Comparison of initial charge/discharge curves of $LiFePO_4$ full batteries assembled with graphite pre-lithiated with Li_2DHBA and graphite pre-lithiated without Li_2DHBA. [148].

significant Mo dissolution in liquid electrolytes.

Park et al. [150] demonstrated that Li_2NiO_2 transforms into an amorphous phase at 3.5 V (Fig. 10b) during initial charging, a potential below that typical of cathodes (~4.0 V). The decomposition products from this transformation provide a discharge capacity of 70–90 mAh g^{-1} in subsequent cycles. The charge and Li^+ generated after delithiation can be utilized for charge compensation at the anode electrode. Decomposition products of Li_2NiO_2, when generated at higher currents, exhibit lower charge transfer resistance, making them suitable for high-current decomposition reactions. Transition metal oxide materials were also found to reduce the need for additional lithium ions sources based on side reactions. Su et al. [151] used $LiCoO_2$ with a 7 wt% Li_5FeO_4 (LFO) additive and a hard carbon anode to form a full cell; its cycling performance improved from $<$ 90% to $>$ 95% after 50 cycles (Fig. 10c). Similarly, cathode additives such as Li_2CuO_2 [152] (Fig. 10d) and Li_6CoO_4 [153] (Fig. 10e) effectively compensate for the irreversible capacity of the anode in LIBs. Although these oxides provide effective compensation for Li^+ loss during the first cycle, most exhibit a relatively small pre-lithium capacity, typically less than 400 mAh g^{-1}. Additionally, the Li_xMO_y series of oxides tends to exhibit multiple voltage plateaus during the decomposition reaction, as demonstrated by Li_5FeO_4 [151]:

$Li_5FeO_4 \rightarrow Li_3FeO_{3.5} + 0.25O_2\uparrow + 2Li^+ + 2e^-$ (plateauI:3.5 V).

$Li_3FeO_{3.5} \rightarrow LiFeO_2 + 0.75O_2\uparrow + 2Li^+ + 2e^-$ (plateauII:4.0 V).

These reactions make the prelithiation process complex and more challenging. Moreover, the use of additives can reduce the volume-specific energy of the battery. Transition metal oxides can also decrease the energy density of the battery, as their decomposition

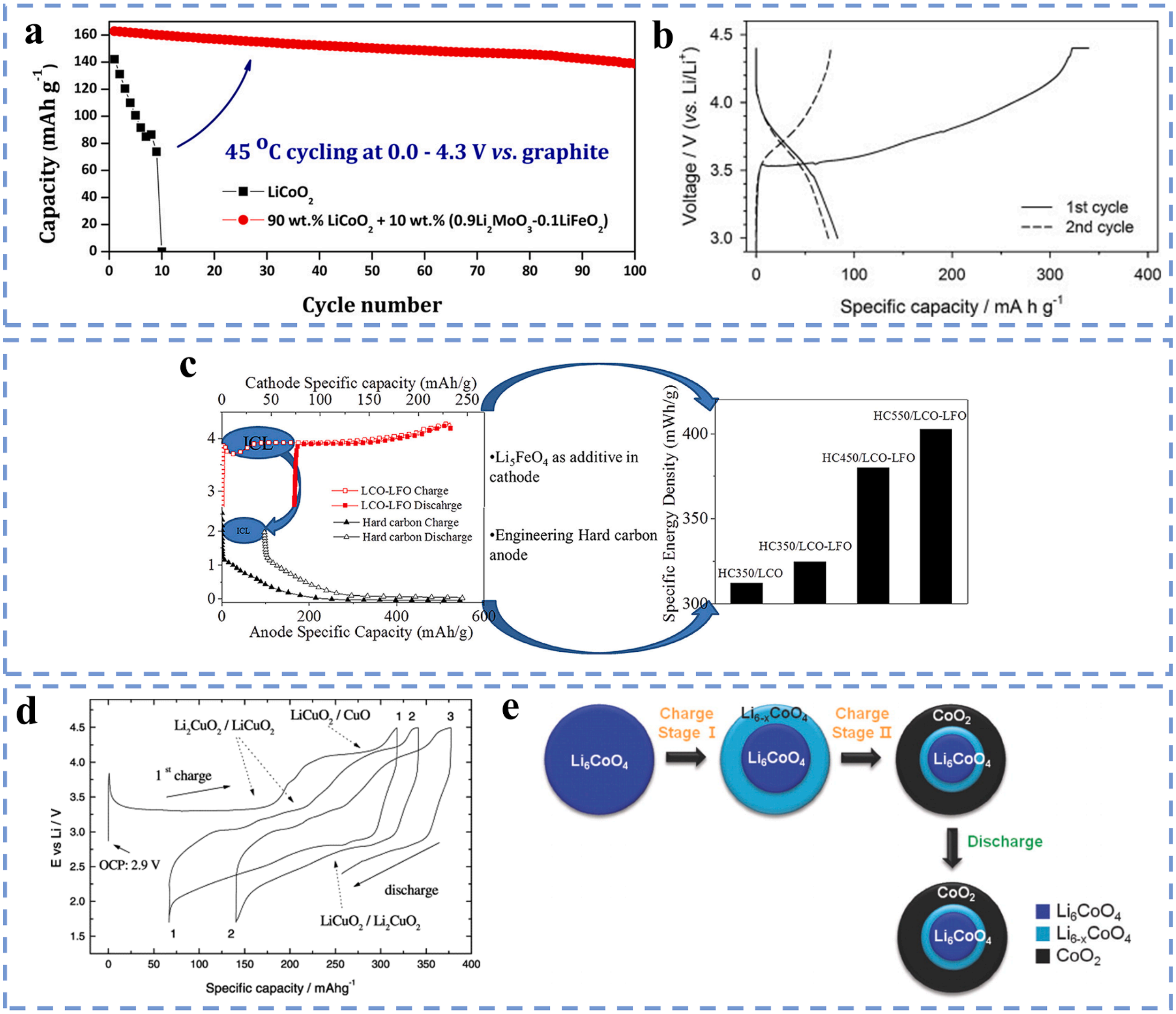


Fig. 10. A) comparison of the cycling curves of licoo$_2$ cathode and $LiCoO_2$ cathode with 10 wt% of $0.9Li_2MoO_3$-$0.1LiFeO_2$ additive in the voltage range of 0.0–4.3 V. [149]. b) The initial charge/ discharge voltage profiles of Li/Li_2NiO_2 cell between 3.0 and 4.4 V [150]. c) Comparison of charging and discharging curves of LCO electrodes containing Li_5FeO_4 additive and LCO electrodes forming a half-cell. [151]. d) The charge/discharge curves for the Li_2CuO_2 electrode were cycled within the voltage range of 1.8–4.5 V at a specific current of 11 mA g^{-1}. [152]. e) Schematic shows the electrochemical reaction of Li_6CoO_4 [153].

products cannot be degraded, limiting their use as anode additives.

In summary, sacrificial salts (e.g., LiN_3, Li_2O, Li_2CO_3, $Li_2C_2O_4$, Li_xMO_y) are used as prelithiation additives to act as a Li^+ donor during the first discharge, compensating for the initial irreversible lithium loss. These salts provide lithium ions, which are then converted to residual gases (N_2, CO or CO_2, among others) that can be removed in subsequent processes. However, the uncontrolled escape of reaction by-product gases could potentially damage the battery. Additionally, the oxides that remain after the decomposition of Li_xMO_y impede the transport of lithium ions. Therefore, it is crucial to identify additives that produce minimal decomposition gases and solid residues and are compatible with existing LIB production processes in future studies.

4.3. M/Li_2X (M = Fe, Co, Ni, Mn, etc., X = O, S, F) nanocomposites

M/LiX (M = Fe, Co, Ni, Mn; X = O, S, N, F, P, etc.) nanocomposites are recognized as a promising category of anode prelithiation reagents. This is due to their ability to provide a substantial amount of lithium 'donor' during the reverse conversion reaction process ($M + LiX \rightarrow Li^+ + LiM$), which has been extensively investigated [154–159]. The formation of metal nanoparticles as reaction products significantly enhances mass and charge transfer processes within the electrode. Among these, M/Li_2O, M/LiF, and M/Li_2S nanocomposites have been most thoroughly studied, while other lithium-metal compounds are less reported and require further research to confirm their prelithiation effects in LIBs.

M/Li_2O-type nanocomposites are particularly favored as prelithiation reagents due to their product composition, Li_2O, resembling the original SEI film, thus avoiding the introduction of new residual compounds. These nanocomposites, formed through the reaction $M_xO_y + 2yLi^+ + 2ye^- \rightarrow xM + yLi_2O$, offer a high theoretical prelithiation capacity of up to 800 mAh g^{-1} during charging. The M_xO_y conversion reaction typically occurs at potentials below 1.2 V and achieves complete delithiation at potentials below 3 V. The typical charge cut-off and discharge cut-off potentials of the cathode material are 4.0 V and 2.5 V (vs. Li/Li^+), respectively, allowing the cathode material to effectively extract Li^+ from the M/Li_2O complex without a reverse reaction. Sun et al. [160] synthesized nano-sized Co/Li_2O composites using a one-step chemical synthesis method. These nano-Co/Li_2O composites displayed lower delithiation potentials and higher delithiation capacities compared to their micron and submicron counterparts, facilitating more efficient Li^+ release. With a 4.8% additive, this nanocomposite achieved a prelithiation capacity of 180 mAh g^{-1} during charging.

LiF/metal nanocomposites are also excellent prelithiation materials for cathodes in LIBs, attributed to their straightforward synthesis route, robust stability under environmental and battery processing conditions, and significant Li^+ donation capacity. Sun's group [161] successfully synthesized LiF/Co nanocomposites through a one-step chemical reaction involving molten lithium metal and CoF (see Fig. 11 a, b). The LiF/Co electrode demonstrated a high charging capacity of 520 mAh g^{-1}, while maintaining a low discharging capacity of 4 mAh g^{-1}. The addition of 4.8% LiF/Co enhanced the initial cycle charging capacity of the cathode by approximately 20 % compared to the original $LiFePO_4$ electrode.

Du et al. [162] developed a robust Fe/LiF/Li_2O nanocomposite for cathode prelithiation, which integrates seamlessly into the conventional electrode fabrication process (Fig. 11c). This nanocomposite exhibits a substantial Li^+ 'donor' capacity during the initial charge/discharge cycle via the inverse conversion reaction: $3Fe + 3LiF + 3Li_2O \rightarrow Fe_2O_3 + FeF_3 + 9Li^+ + 9e^-$. The Li^+ 'donor' capacity reaches 523 mAh g^{-1}, which is three times higher than that of existing cathode materials. Additionally, with the incorporation of 4.8 wt% Fe/LiF/Li_2O, the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ electrode experiences a 16–20% enhancement in specific capacity compared to the original cathode during the initial charging. The environmental stability of these nanocomposites was confirmed through static experiments conducted in ambient air (20% humidity), indicating favorable performance under various conditions.

Li_2S, as a high-capacity anode prelithiation material for existing LIBs, must overcome several challenges [163–165]: 1) its incompatibility with conventional carbonate-based electrolytes; 2) the diffusion of intermediate polysulfides and the low electrical conductivity of Li_2S; 3) instability and reactivity with moisture when exposed to air. By mixing ultrafine Li_2S with metal particles, the lithium extraction mechanism shifts from a decomposition reaction to a transformation reaction, alleviating the incompatibility with carbonate-based electrolytes. The electrochemical lithiation and delithiation potentials for the conversion of Li_2S to polysulfides occur at less than 2 V and 3 V, respectively. This makes the transformation reaction in Li_2S/metal composites a unidirectional lithiation reaction, achieving maximum lithium capacity of the prelithiation reagent.

Sun et al. [166] synthesized Li_2S/metal (Li_2S/Co and Li_2S/Fe) nanocomposites using metal sulfide particles (CoS_2 and FeS_2) and lithium metals through a chemical conversion reaction: $Co + 2Li_2S \rightarrow CoS_2 + 4Li^+ + 4e^-$, $Fe + 2Li_2S \rightarrow FeS_2 + 4Li^+ + 4e^-$ (Fig. 11d). These nanocomposites immobilize polysulfide intermediates, preventing their irreversible reaction with the carbonate electrolyte. The Li_2S/Co nanocomposites exhibit a charging specific capacity of 683 mAh g^{-1}, surpassing previously reported Li_2O/Co and LiF/Co nanocomposites. Serving as prelithiation additives for existing cathodes, these nanocomposites enable the extraction of nearly all lithium ions when charged below the cutoff potential of 0 V. Similarly, the FeS_2/Fe nanocomposites, prepared in a similar manner, demonstrate a high capacity of 480 mAh g^{-1} in the initial charge/discharge cycle, exhibiting exceptional prelithiation efficiency.

M/Li_2X pre-lithiation additives serve as stable lithium donors, leveraging their high specific capacity and large potential hysteresis of the conversion reaction to achieve high prelithiation efficiency. Utilizing this type of cathode prelithiation additive can lead to a significant increase in specific capacity and energy density of full battery. From the above research, it can be reasonably concluded that the nanocomposites prepared from other metals (V, Ni, Mn, Sn) and Li_2X also share a similar conversion reaction mechanism and are very promising materials for high capacity prelithiation.

5. Devices-integrated prelithiation strategy

The storage of lithium resources in a complete battery system is concentrated in two main components: the electrode materials and the electrolyte solution. The lithium in the electrode material provides the conversion energy, but some energy leads to capacity decrease due to lithium loss at the anode. Thus, prelithiation of both the anode and cathode can directly address issues of lithium inactivation and loss. Additionally, the lithium resources in the electrolyte solution can effectively alleviate the concentration differences and polarization of lithium ions during the insertion and extraction processes between the cathode and anode. However, a significant portion of lithium loss at the anode occurs due to the decomposition of the electrolyte solution. From the perspective of battery system design, a comprehensive analysis of lithium replenishment through electrolyte, electrode binder, and separator modifications is crucial for realizing efficient inter-electrode lithium conversion storage.

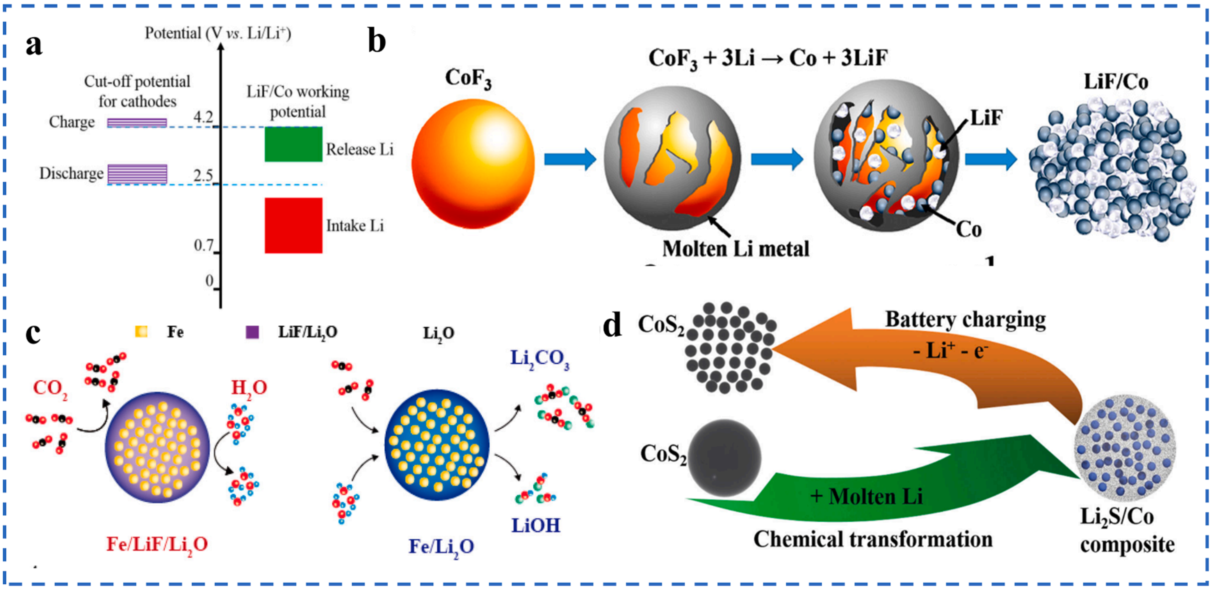


Fig. 11. A) the left figure illustrates the cutoff potential for current cathodes, whereas the right depicts the ideal delithiation and lithiation potential for lif/co nanocomposites. [161]. b) Formation process of LiF/Co nanocomposites presented in a flow chart. [161]. c) Chemical stability comparison of Fe/LiF/Li_2O and Fe/Li_2O Nanocomposites in ambient air [162]. d) The schematic of the chemical synthesis of a Li_2S/Co composite and the electrochemical extraction of Li^+ during the battery charging process. [166].

5.1. Electrolyte additive prelithiation

Replenishing lithium via electrolyte additives offers a novel approach to prelithiation. The use of film-forming additives in the electrolyte, such as vinylene carbonate (VC), has significantly enhanced the cycling performance of graphite and silicon anodes [153,167]. Similarly, fluoro-substituted vinylene carbonate has improved the performance of silicon anodes [168,169]. Additionally, the inclusion of a small quantity of lithium bisoxalate borate in the electrolyte enhances the interfacial structure of $LiNiO_2$-graphite materials without altering the electrolyte's characteristics [170]. This promotes the formation of a uniform, dense, mechanically sound, and structurally solid SEI film, indirectly replenishing the lithium in the batteries and leading to an overall improvement in battery performance.

Wang et al. [171] developed a new electrolyte, 2 M $LiBH_4$/THF (tetrahydrofuran)-MeTHF (2-meth-yltetrahydrofuran) (abbreviated as LBH), which is fluoride-free and used for micro-Si anode-2 M $LiBH_4$/THF-MeTHF. This electrolyte protects the internal conductive network by chemically prelithiating the primary oxide layer with reducing $LiBH_4$, mitigating the formation and accumulation of SEI. Compared to conventional electrolytes, LBH electrolytes can partially prelithiate SiO_x and limit the formation and accumulation of SEIs due to their strong reducing properties. A half-cell, assembled using an 80 wt% Si anode in a fluoride-free electrolyte, exhibited a high reversible capacity of 2900 mAh g^{-1}, an ICE of 94.7%, and a capacity retention of 94.3% after 100 cycles at 0.2C (Fig. 12a). Zhou et al. [172] developed an electrolytic cell consisting of a cupro-corrosion-type anode half-cell in an aqueous electrolyte and a lithium-cell-type positive half-cell in a gel polymer electrolyte. They carried out rapid (4.2 h) prelithiation of binder-free silicon electrodes using this electrolytic cell and successfully used a lithium-containing aqueous solution as both the electrolyte and the lithium source. Utilizing the prelithiated Si electrode as the anode and an ACNTs@MnO_x composite on aluminum foil as the positive electrode, the specific energy of the prelithiated MnO_x/Si lithium-ion full cell remained at 138 Wh kg^{-1} at a specific power of 1710 Wh kg^{-1}. This innovative prelithiation technique is not only safer and more environmentally friendly but also presents a new approach to the efficient use of lithium resources, such as extracting lithium from saline lakes and

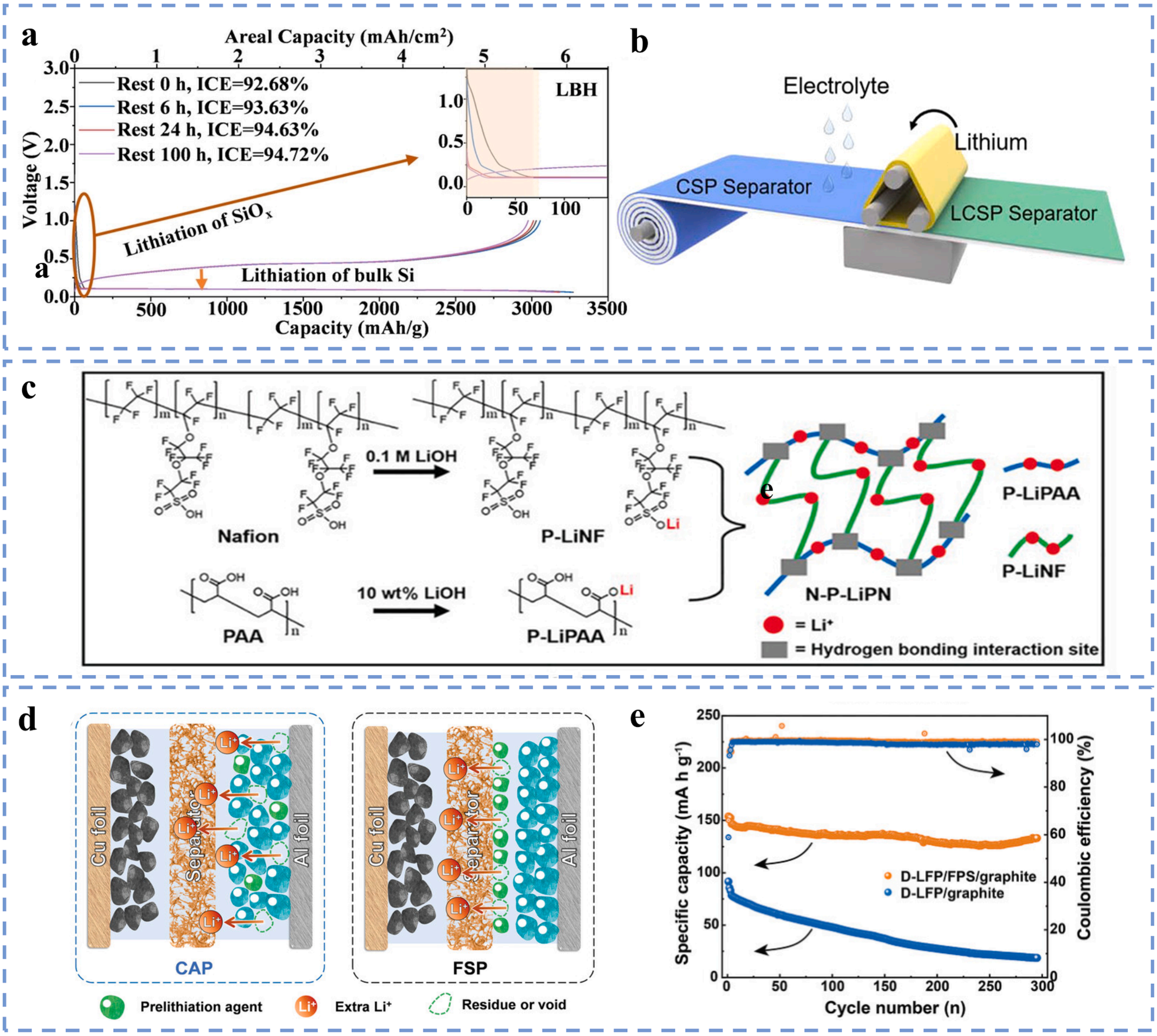


Fig. 12. A) the figure shows a comparison of the charge–discharge curves of bulk Si after lithiation with LBH electrolyte at different resting times. The inset shows a magnified view of the curve at the start of lithiation. [171]. b) Schematic of the scalable LCSP separator manufacturing process. [176]. c) Schematic of preparing the N-P-LiPN binder [174]. d) Additional Li^+ are released from the prelithiated separator during the CAP using Li rich or overlithiated cathode additives and during the FSP using a functional separator. [177]. e) Comparison of the cycling stability for the regenerated cell with and without FPS [178].

recycling lithium batteries in aqueous solutions.

5.2. Binder-modified prelithiation

Binders are a crucial component of LIBs as they secure and maintain the structural integrity of both the cathode and anode materials, the electrolyte, and the separator. The performance of binders significantly affects the lifetime of LIBs. Prelithiated binders have been shown to improve the electrochemical performance of electrodes. Prelithiation of binders enhances the Li^+ transport rate across them while preserving the multitude of functional groups that facilitate subsequent lithiation reactions. Selvamani et al. [173] achieved the lithiation of perfluorosulfonated copolymers through a simple alkali treatment, which displaced acidic protons. They used these copolymers to replace the original conductive binder in nickel-rich positive electrodes. The electrode treated in an ethanol medium exhibits an extremely high reversible capacity of approximately 190 mAh g^{-1} and a capacity retention of 82% after 100 cycles at a rate of 0.5 C. By adjusting the binder composition to control the deformation of the electrode material and inhibiting the continuous formation of the solid-electrolyte interface (SEI) film through functional group interactions, prelithiation controls the depletion of excess lithium ions.

The objective of prelithiation can be achieved by modulating the binder composition to exploit the interaction of functional groups that can limit the deformation of the electrode material, inhibit the continuous formation of the SEI film, and control the consumption of excess lithium sources. Li et al. [174] devised a trifunctional network binder (N-P-LiPN) through hydrogen bonding, incorporating partially lithiated hard polyacrylic acid (P-LiPAA) as the backbone and soft Nafion as the buffering agent (depicted in Fig. 12c). The hard P-LiPAA chains, featuring numerous carboxylate groups, confer strong adhesive strength and exceptional mechanical properties. Concurrently, the soft P-LiNF chains, abundant in sulfonic acid groups, facilitate accommodation of the significant volume change of the Si anode. Additionally, Li^+ migration occurs through the lithiated groups of N-P-LiPN, significantly enhancing the ionic conductivity of the silicon anode. Qiu et al. [175] synthesized lithium carboxymethyl cellulose (CMC-Li) using a new process (lithium ethanol), which offers better suspension and dispersion properties than conventional CMC-Na. This material is also chemically stable and does not react with the electrolyte, resulting in a 2% increase in initial cycle efficiency and approximately 12% longer cycle life.

5.3. Separator-modified prelithiation

Introducing pre-lithium additives directly onto the cathode side is an effective prelithiation strategy. However, the decomposition of these additives during the first charge can lead to the formation of poorly conducting residues or voids, caused by the escape of generated gases. This impedes charge transfer and degrades the cathode structure [44]. Additionally, additives that are rich in lithium often prove unstable in air and fail to meet the necessary production requirements for cathodes. To address these challenges, researchers have coated the active substance onto the separator and integrated it into the full cell, significantly reducing disruptions in the lithium ions' conduction path and inhibiting catalytic reactions with the active substance, thereby preventing residue formation.

Rao et al. [176] modified a commercial separator with Li_2S/Co nanocomposites to prevent damage to the positive electrode caused by the generation of additive residues during electrode production (see Fig. 12b). The Li_2S/Co coating stabilizes active lithium ions during charging, resulting in a delithiation capacity of 993 mAh g^{-1}. When paired with a graphite full cell with $LiFePO_4$, the reversible capacity increased from 112.6 mAh g^{-1} to 150.3 mAh g^{-1}, representing a 29.5 % increase in energy density. Guo's group [177] designed a functionalized prelithiation separator (FSP) (illustrated in Fig. 12d). The FSP method involves applying the Li_5FeO_4 (LFO) prelithiation reagent to the separator, thus avoiding the introduction of highly alkaline substances into the cathode slurry. This approach mitigates the risk of slurry gelling and protects the cathode electrodes from damage. Antifluorite-LFO is affixed to one side of the membrane as a prelithiation reagent, providing a substantial irreversible capacity of 701 mAh g^{-1} through a four-electron redox reaction during the initial formation process. By employing a functional separator, the reversible capacity of the NCM811||SiO_x/G full cell is enhanced by over 40 %. This technique demonstrates high adaptability to electrode preparation and cell manufacturing processes, enabling the replenishment of anode lithium loss and the reabsorption of anode lithium to inhibit localized over-lithiation and lithium dendrite formation simply by adjusting the cell voltage. Fan et al. [178] coated a prepared $Li_2C_2O_4$/CMK-3 composite on a commercial separator as a "sacrificial salt" and reduced the decomposition potential of $Li_2C_2O_4$ to below 4.5 V by ultrasonic mixing and recrystallization. When this functionalized separator (FPS) was assembled into a full cell with recycled $LiFePO_4$ as the cathode electrode, it was found that the D-LFP/FPS/graphite full cell still had a high specific capacity of 146.7 mAh g^{-1} and a high capacity retention rate of 90.7 % after 292 cycles (Fig. 12e), compared with the values of 78.5 mAh g^{-1} and 18.7 % respectively for the full cell without FPS. The lithium-rich additive coated on the separator partially solves the problem of cathode prelithiation. Due to the smaller contact angle between the active substance and the separator, the charge transfer rate is also somewhat improved.

Binder, separator-modified, and electrolyte addition prelithiation technologies as lithium replenishment strategies provide new ideas for prelithiation. Due to their minimal addition and low lithium content, binder additives have less impact on the initial efficiency loss. The addition of lithium salt in the electrolyte can effectively reduce polarization. The introduction of a small amount of lithium additive can inhibit the occurrence of side reactions and enhance the electrochemical performance of the battery. Separator-modified prelithiation, a derivative of lithium-rich "sacrificial salt" for cathodes, partially solves the damage to the cathode structure caused by its decomposition products. The manufacturing process is simple and easy to scale up. Developing new binders and electrolytes suitable for the battery system is crucial for advancing prelithiation technology. However, the use of modified electrolytes, binders, and separators in lithium supplementation is less common in current commercialization. Therefore, researching and developing new systems to replace existing mature processes presents a significant challenge.

6. Conclusions and perspectives

Most prelithiation methods are currently in the laboratory research stage, and the industry has not yet developed a mature and controllable prelithiation process compatible with existing LIB production lines. This review systematically discusses the challenges faced by LIBs during cycling, including low ICE, poor capacity retention, and short cycle life. It also analyzes the reasons for the loss of active lithium, based on existing literature. From the perspective of prelithiation mechanisms, it examines factors such as contact surfaces and electron channels that may impact the prelithiation effect and summarizes the application of various advanced characterization tools in prelithiation technology. Various prelithiation strategies based on modifications to the anode, cathode, electrolyte, binder, and separator have been gradually explored, each demonstrating diverse lithiation mechanisms. As illustrated in Fig. 13, this review compares the advantages and characteristics of various prelithiation strategies (anode-directed prelithiation, cathode-assisted prelithiation, and device-integrated prelithiation) across six aspects: prelithiation control precision, electrode stability, production cost, replenishment capacity, safety, and process compatibility. In addition, this review discusses the potential future development trends of prelithiation technology and the feasibility of its commercial application, considering the various challenges associated

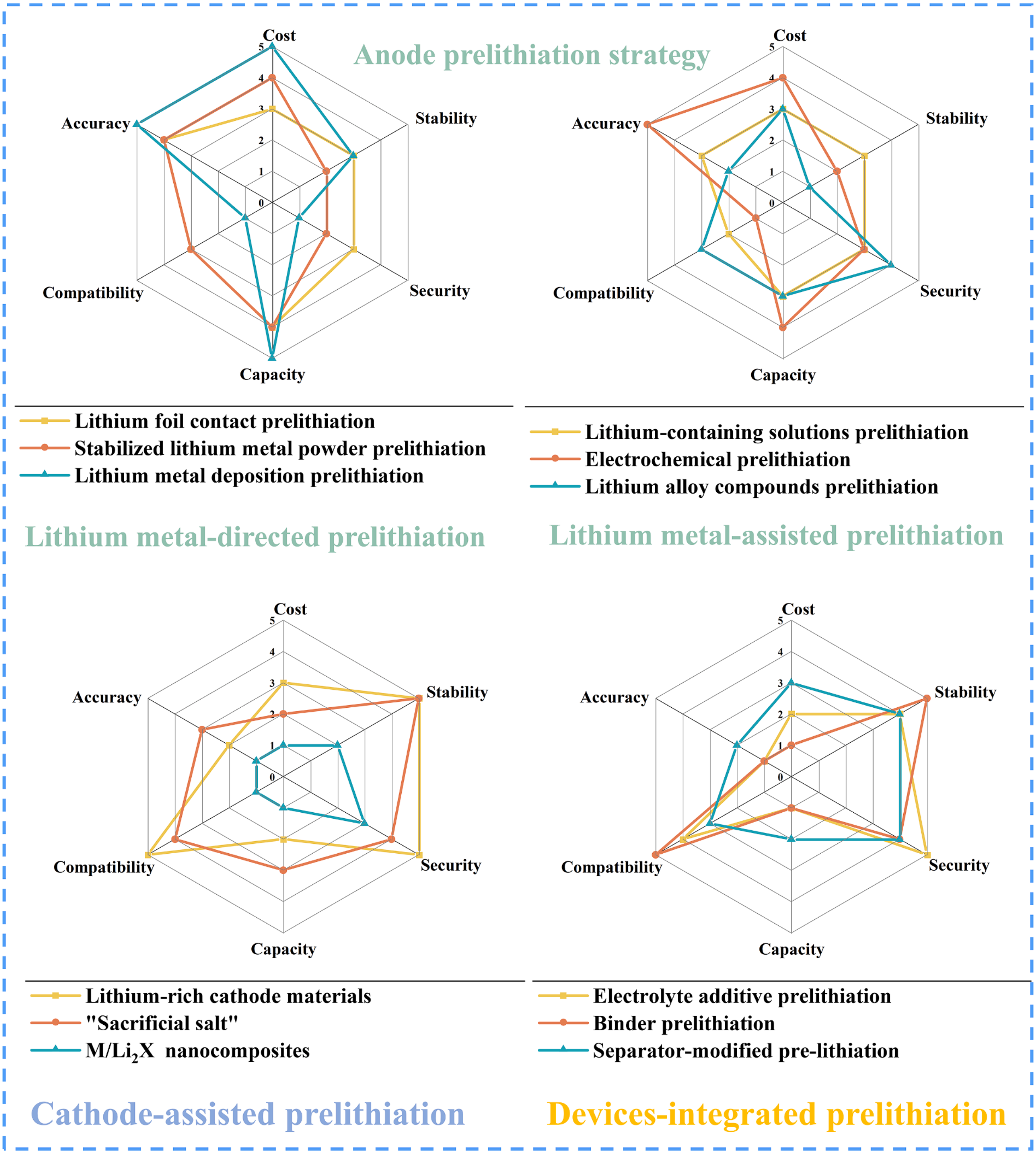


Fig. 13. Comprehensive performance comparison of various prelithiation strategies.

with different prelithiation strategies.

6.1. Commercialization analysis of prelithiation

One of the primary challenges in the commercialization of lithium metal contact prelithiation is the difficulty and high cost of manufacturing ultra-thin lithium foils. It is recognized by both academia and industry that the thickness of lithium metal foils used for prelithiation should be less than 5 μm. However, there is currently no mature production process available on the market for producing lithium foils with a thickness of less than 5 μm. The rolling process, which is the most commonly employed technique for thinning lithium metal foil, often leads to damage due to the pressure exerted on the surface oxide film of the material. This can result in both surface and internal structural damage to the lithium foil. The SLMP prelithiation method has lower environmental requirements due to its external coating of a stable oxide film. However, the high cost of SLMP restricts its large-scale application. Additionally, ensuring the uniform dispersion of SLMP within the anode, and its compatibility with the electrolyte and binder, remain significant challenges. Methods such as lithium electroplating and vacuum thermal evaporation lithium plating for the deposition of lithium metal are highly demanding environmentally. The subsequent battery assembly process must be conducted under a dry and inert gas atmosphere, which significantly increases the cost of prelithiation.

The lithium metal-assisted prelithiation strategy relies on external current control, solution dispersion properties, interfacial modification, and other measures to enhance the prelithiation process in terms of precision, uniformity, stability, and process compatibility. In commercial applications, the electrochemical prelithiation process facilitates a roll-to-roll prelithiation process, where an appropriate amount of commercial electrolyte is placed between the lithium foil and the anode electrode. This setup simulates the presence of a separator under actual battery operating conditions, thereby generating an artificial SEI film. Prelithiation using lithium-containing solutions, with common chemical solvents such as naphthalene, biphenyl, tetrahydrofuran, and n-butyllithium, is limited to prelithiation of electrodes with lower redox potentials. The range of application for these methods is narrow. Additionally, these solvents dissolve lithium slowly, are costly, and the instability of the products post-lithiation renders them unsuitable for large-scale application. Prelithiation through lithium alloy compounds involves using a lithium alloy coating to compensate for lithium loss in the anode during the discharge process. However, this approach sacrifices the volume-specific capacity of the anode and introduces additional processing challenges. Moreover, the modified lithium alloy coating is highly susceptible to reactions with external elements, requiring the subsequent battery assembly to be performed in a dry, inert atmosphere. For commercialization, it is also necessary to address the compatibility of the lithium alloy coating with existing manufacturing processes and to reduce the costs of synthesis.

Lithium-rich cathode materials are known for their low lithium storage capacity. However, they are compatible with the existing electrode paste manufacturing process and maintain a stable electrode structure, making them widely used in ternary cathode materials. However, the positive lithium-rich substrate material exhibits limited lithium storage capacity and is not suitable for pre-lithiation of silicon-based and conversion reaction class anode materials. This substrate is typically used for pre-lithiation of graphite and lithium titanate anode materials. “Sacrificial salts” are often added to the cathode during the slurry material preparation stage, and the electrodes post-pre-lithiation are highly sensitive to humidity. Therefore, it is necessary to upgrade the humidity control systems in LIB manufacturing plants. The decomposition of “sacrificial salt” often generates oxidation by-products that are difficult to decompose and gases. Therefore, controlling the generation of oxidation products during industrialization is crucial to prevent irreversible damage to the electrodes. Conversely, “sacrificial salt” prelithiation technology is more suitable for pouch batteries equipped with gas collection chambers that can collect the residual gases from oxidative decomposition. The process of preparing prelithiation additives based on the reversible conversion reaction requires melting lithium to synthesize M/Li_2X additives, which is costly and poses significant safety risks. The future development of synthesizing M/Li_2X materials without melting lithium presents greater prospects for advancement [179].

The primary role of binders and electrolyte additives containing minimal lithium is to stabilize the structure of the electrode and the stability of the reaction, inhibiting the occurrence of side reactions, among other functions. These two types of prelithiation technologies are often applied in conjunction with other prelithiation processes. Separator-modified prelithiation, an extension of cathode-assisted prelithiation, avoids damage to the electrode from additive oxidation decomposition products and is also compatible with existing processes. However, the current PP/PE separators have low porosity, poor electrolyte wettability, and slow lithium ion transport rates, which are challenging to align with the current prelithiation processes. Identifying a separator with high porosity and uniform pore size distribution is crucial, such as one made from electrostatically spun nanofibers. Moreover, commercial applications also necessitate the development of a supportive system comprising electrolytes, binders, and new separators, which requires substantial initial investment in research and development, presenting a significant challenge for enterprises.

6.2. Challenges and perspectives of prelithiation

Although prelithiation technology has achieved notable success in offsetting irreversible capacity loss and enhancing energy density, the practical application of prelithiation technology has become feasible due to the in-depth study of its mechanisms and advancements in battery equipment. However, several key issues and challenges still need to be addressed for its industrial applications:

1. Precision of prelithiation: The precision of prelithiation is a crucial parameter that affects electrode performance. Controlling the amount of lithium ions introduced is essential. In commercial applications, improving lithium utilization can be approached from two angles:

Calculating lithium requirements: Based on the irreversible capacity loss and the utilization rate of active lithium in the early stages of LIBs, it is vital to precisely calculate the quality of sacrificial lithium sources. These sources should be added to the electrode surface or internally by various prelithiation technologies to achieve precise lithium replenishment of anode materials. Techniques such as controlling lithium deposition thickness and the quantitative addition of SLMP are used.

Enhancing utilization of sacrificial lithium sources: Not all lithium from sacrificial sources is effectively utilized. When using SLMP, the unconverted lithium, known as “dead lithium,” loses its electronic conductivity and accumulates around the anode interface. This accumulation hinders proton/charge transfer reactions, leading to increased polarization and lithium plating during battery operation. To mitigate this issue, it is necessary to upgrade the prelithiation process. This includes constructing a stable SEI at the electrolytic interface to prevent new SEI formation due to electrolyte dissolution and reactions with reactive lithium and designing suitable interfaces to increase electrical conductivity.

2. Incompatibility between lithium replenishment additives and electrolyte: Lithium-containing solutions can undergo prelithiation by selecting a suitable solvent based on its redox potential and conducting the corresponding electrochemical reaction. The electrochemical prelithiation method allows for precise control of the prelithiation reaction by adjusting the charge and potential through the applied current, suitable for agents with high redox potential. However, the reagents used in SLMP lithium replenishment, chemical prelithiation, and electrochemical prelithiation methods are often highly reactive. Most of these reagents react violently with carbonate electrolytes, leading to electrolyte degradation and decreased battery capacity. It is crucial to develop chemically stable prelithiation reagents that are compatible with current battery manufacturing processes. This includes technologies for prelithiation reagent surface passivation. Additionally, developing an electrolyte system that is electrochemically stable, matches the additive, and has a specific electrochemical window is also necessary to accommodate new lithium replenishment additives.

3. Volume expansion after prelithiation: The prelithiation process in high-capacity electrode materials can lead to volume expansion, which results in particle defects, electrode cracks, and chalking. For instance, during prelithiation, lithium alloy compounds form at the interface of alloy-type (silicon/silicon oxide) anode materials, causing significant volume changes. Similarly, lithium-rich cathode materials experience volume expansion during lithium embedding, which can compromise the stability of the electrode structure and reduce the service life in subsequent cycles. Although the prelithiation strategy can address the issue of low ICE and mitigate irreversible lithium loss, it cannot fundamentally resolve the structural defects in electrodes and materials. Therefore, it is essential to design stable structures and optimize the performance of electrode materials before implementing the prelithiation process to fully leverage the benefits of this technology.

4. Poor environmental stability of the electrode after prelithiation: Due to not reaching the equilibrium state, reaction products obtained from electrochemical prelithiation exhibit a high degree of instability. Additionally, a self-discharge effect occurs and significantly reduces the effectiveness of prelithiation without an external circuit. Interface

modification of anode materials involves adding lithium-rich substances to the interface to supplement the irreversible capacity during the initial discharge process. However, the resulting alloy interface or artificial SEI film is extremely unstable in air. Lithium-rich compound additives can provide sufficient lithium ions for the prelithiation reaction. However, after fully reacting, they produce by-products that are difficult to decompose, generating gases or oxides, which inevitably affect the stability of the electrodes. Moreover, lithiation reaction products are generally sensitive to moisture and air; thus, any subsequent work after prelithiation requires operation in an inert atmosphere, increasing the cost of industrial applications.

In summary, this paper reviews the development process of various prelithiation strategies and their respective advantages and challenges, based on the issues associated with the commercialization of the prelithiation process. Prelithiation technology focuses on controlling lithium replenishment capacity and analyzing the feasibility of commercialization. Furthermore, the impact of prelithiation on the electrode structure, in terms of the reaction mechanism, precision, and stability of the subsequent electrode structure, will be significant in scientific research. In the future, the importance of prelithiation technology is expected to grow with the advancement of next-generation large-capacity anode materials. To further advance prelithiation technology, it is necessary to explore new physical and chemical prelithiation strategies, such as electrospray technology, plasma spraying technology, and new lithiation reagents. Additionally, while some prelithiation methods are still applied in laboratory settings or small-scale pilot production, transitioning these methods to large-scale production is crucial. This transition necessitates higher precision, process compatibility, and cost-effectiveness in the prelithiation strategy.

CRediT authorship contribution statement

Bo Jin: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Keyu Zhang:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Geng Gao:** Writing – original draft, Formal analysis. **Qing Zhao:** Writing – original draft, Formal analysis. **Xinyu Jiang:** Writing – original draft, Formal analysis. **Dingfang Cui:** Writing – original draft, Formal analysis. **Keqi Chen:** Writing – original draft, Funding acquisition, Formal analysis. **Xiang Lin:** Resources, Investigation, Formal analysis. **Liuliu Liu:** Writing – original draft, Formal analysis. **Rui Yan:** Writing – original draft, Resources, Formal analysis. **Bin Yang:** Resources, Conceptualization. **Yaochun Yao:** Writing – review & editing, Project administration, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (Grant No. 52104302), the project of Yunnan Fundamental Research Projects (Grant No. 202101BE070001-020, 202202AB080013, 202201AT070098, 202401AS070069, 202402AF080003), Analysis and Testing Foundation of Kunming University of Science and Technology (Grant No. 2023 M20222202139), National Undergraduate Innovation and Entrepreneurship Training Program Project in Key Areas (Project No. 202310674002).

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