

## REVIEW

# Lithium sulfide: a promising prelithiation agent for high-performance lithium-ion batteries

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## Abstract

Lithium-ion batteries are widely used in portable electronics and electric vehicles due to their high energy density, stable cycle life, and low self-discharge. However, irreversible lithium loss during the formation of the solid electrolyte interface greatly impairs energy density and cyclability. To compensate for the lithium loss, introducing an external lithium source, that is, a prelithiation agent, is an effective strategy to solve the above problems. Compared with other prelithiation strategies, cathode prelithiation is more cost-effective with simpler operation. Among various cathode prelithiation agents, we first systematically summarize the recent progress of Li<sub>2</sub>S-based prelithiation agents, and then propose some novel strategies to tackle the current challenges. This review provides a comprehensive understanding of Li<sub>2</sub>S-based prelithiation agents and new research directions in the future.

## KEYWORDS

Li-ion batteries, prelithiation, Li<sub>2</sub>S, prelithiation agent, metallothermic reduction reaction

## 1 | INTRODUCTION

Global climate crisis from excessive consumption of traditional fossil fuels has expedited the development of renewable energy, including nuclear energy, solar energy, tidal energy, wind energy, biomass energy, hydrogen

energy, etc.<sup>1–8</sup> However, renewable energy suffers from its volatility, intermittency, and randomness, which are the bottlenecks of replacing traditional fossil fuels. Therefore, a cost-effective, safe and efficient energy storage fashion is required to balance the irregularity of renewable energy and the diversity of electricity consumption.<sup>9–14</sup> Among various energy storage fashions, lithium-ion batteries (LIBs) have been widely used in portable electronics

Junkang Huang and Weifeng Li contributed equally to this study.

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and electric vehicles due to their advantages of high energy density, long service life, and low self-discharge.<sup>15–19</sup>

Concerning excessive carbon emission, the electric vehicle market has grown prosperously under the support of policy and funding from governments.<sup>20–25</sup> Meanwhile, requirements for better performance, from perspectives of energy density, cycle stability, and safety, are also imposed on LIBs. As we know, partial  $\text{Li}^+$  from the cathode is consumed to form the solid electrolyte interface (SEI) on the anode surface during the first few charging processes.<sup>26</sup> The loss of active  $\text{Li}^+$  is irreversible, directly leading to dropped energy density and deteriorated cycle life.<sup>27</sup> Compared with an irreversible lithium loss of 5%–10% for graphite anode, the situation gets even worse for conversion-type and alloy-type anode materials of higher capacity. For example, the silicon anode with a theoretical capacity of 3 579 mAh/g, suffers from a lithium loss as high as 35%.<sup>28–34</sup> Due to huge volume changes, unstable SEI formed during the first cycle still continuously consumes  $\text{Li}^+$  in the following cycles, leading to the poor cycling life. The huge  $\text{Li}^+$  loss due to the SEI formation, marked by a low Coulombic efficiency (CE), greatly limits the application of high-capacity anode materials. Despite intensive investigations on novel electrodes, electrolytes, and additives, prelithiation is still the most effective and direct way to enhance the initial CE and compensate for the irreversible lithium loss.<sup>35–46</sup> The central issue of prelithiation is to compensate for the lithium loss during SEI formation from an external lithium source, that is, prelithiation agents, rather than cathode materials. Aiding by prelithiation agents, both energy density and cycle stability can be improved. As reported by Zhan et al., the specific capacity of the  $\text{LiFePO}_4$  ( $\text{Li}_2\text{S}$ )/C battery is 140 mAh/g after the first cycle, which is 12 mAh/g higher than that of  $\text{LiFePO}_4$ /C battery. In addition, the  $\text{LiFePO}_4$  ( $\text{Li}_2\text{S}$ )/graphite full cell shows a CE of almost 100% in the following cycles at 0.2C.<sup>47</sup> Therefore, exploring effective prelithiation agents is one of the key strategies to improve the energy density and cycle life of next-generation LIBs.

This review introduces the principle and classification of prelithiation agents for LIBs and highlights the theoretical research and current problems. It also summarizes and discusses the research progress of prelithiation agents, with a focus on  $\text{Li}_2\text{S}$ -based prelithiation agents. Finally, some perspective strategies are proposed to tackle current challenges.

## 2 | PRELITHIATION

The CEs of the anode materials during the first few cycles are always lower than 100% due to the discrepancy between charge capacity and discharge capacity.

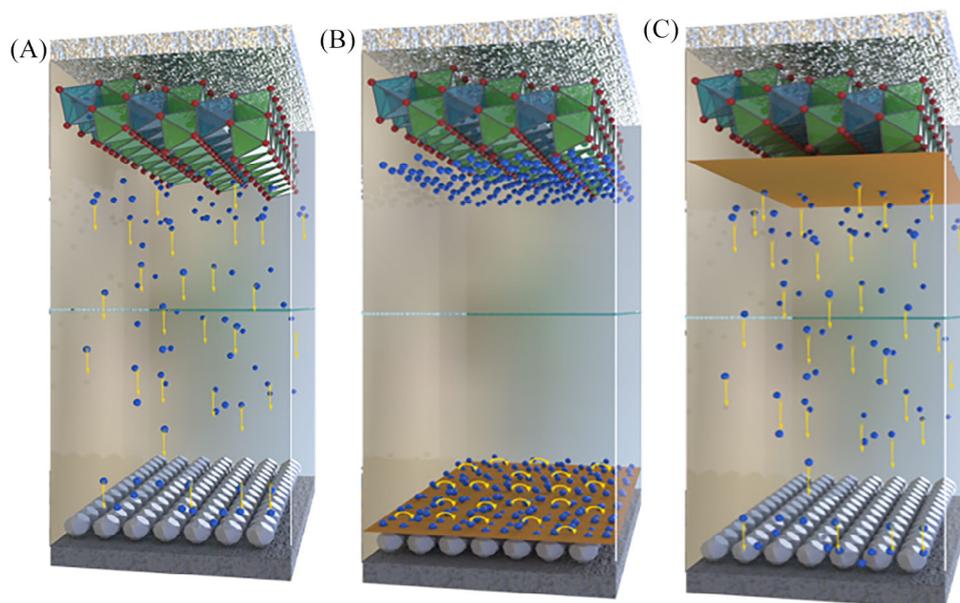
The extra charge capacities in the first few cycles correspond to SEI formation.<sup>48–52</sup> The prelithiation agents as extra lithium sources irreversibly release active  $\text{Li}^+$  in the first cycle, during the process of which the unstable electrolyte decomposes by intaking  $\text{Li}^+$  to form Li-containing compounds on the anode surface (Figure 1A). These compounds, including  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_x\text{PF}_y$ ,  $\text{Li}_x\text{SiF}_y$ ,  $\text{Li}_x\text{SiO}_y$  and lithium alkyl carbonate components, are so thermodynamically stable that the SEI formation is irreversible.<sup>53,54</sup> As a passivation layer, SEI is essentially an electronic insulator but an excellent  $\text{Li}^+$  conductor. This property allows free  $\text{Li}^+$  shuttle, while avoiding the direct contact between the electrolyte and the anode material, which prevents further degradation of anode materials in the following cycles. Therefore, SEI is an indispensable part of maintaining the LIBs' stability. However, the SEI formation is at the expense of a definite  $\text{Li}^+$  source from cathode material, directly leading to a drop in the energy density of the full cell. Based on this fact, the prelithiation concept is raised, that is, utilizing a lithium source outside the cathode to release  $\text{Li}^+$  irreversibly to compensate for the  $\text{Li}^+$  loss during SEI formation. As shown in Figure 1B,C, either prelithiation agents on the anode side or the cathode side provide extra  $\text{Li}^+$  resources for the SEI formation without consuming active  $\text{Li}^+$  in the cathode materials. The prerequisite of prelithiation agents lies in their lower delithiation/lithiation potentials than those of cathode materials, resulting in complete  $\text{Li}^+$  release without recovery.<sup>55–59</sup>

## 3 | PRELITHIATION TYPE

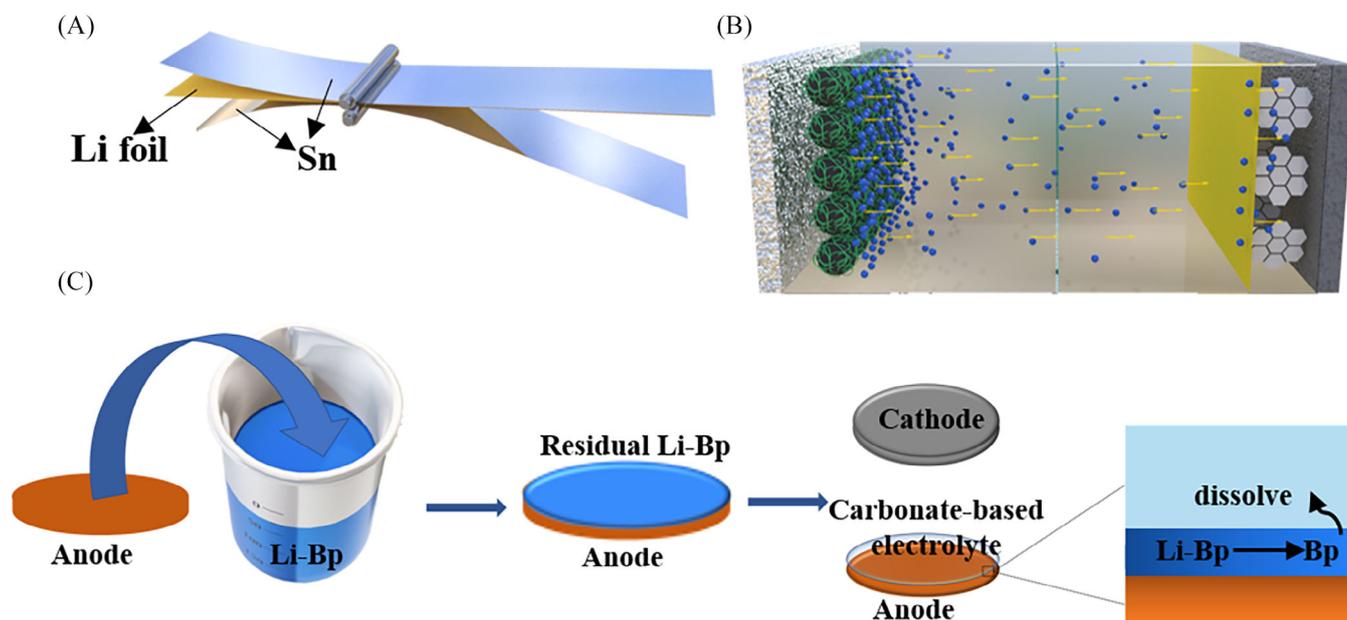
According to the mechanism, prelithiation can be divided into three categories: mechanical prelithiation, electrochemical prelithiation, and chemical prelithiation.

### 3.1 | Mechanical prelithiation

The mechanical prelithiation is to make physical contact happen directly between anode materials and lithium metal (Figure 2A).<sup>60–64</sup> The merits of lithium metal lie in its high prelithiation capacity of over 3 860 mAh/g and zero residues after prelithiation.<sup>65</sup> However, it is difficult to control the prelithiation degree of lithium metal foil. Compared with lithium metal foil, the form of lithium metal powder ensures the precise control of prelithiation degree. Moreover, the high surface area of lithium metal powder facilitates the prelithiation more effectively. The chemical activity of lithium metal powder, however, is too high to accommodate the practical battery assembly process. Recently, stabilized lithium metal powder, with



**FIGURE 1** (A) SEI formation on anode surface without prelithiation, (B) with anode prelithiation agent, (C) with cathode prelithiation agent. SEI, solid electrolyte interface.



**FIGURE 2** Process of (A) mechanical prelithiation, (B) electrochemical prelithiation, and (C) chemical prelithiation.

Li-containing inorganic salts or organic substance as a protective layer, is considered a promising mechanical prelithiation agent.<sup>66</sup>

### 3.2 | Electrochemical prelithiation

Electrochemical prelithiation can be simply expressed as the first discharge process of anode materials in the half

cell (Figure 2B). During electrochemical prelithiation, SEI is formed on the anode material surface by consuming  $\text{Li}^+$  resource from Li metal.<sup>67–71</sup> Compared with uncontrollable mechanical prelithiation, short-circuiting risk is eliminated. Moreover, the prelithiation rate and prelithiation degree can be controlled precisely in a mild way by adjusting the electrochemical prelithiation parameter. Similar to mechanical prelithiation, electrochemical prelithiation is restricted to an inert atmosphere due to the

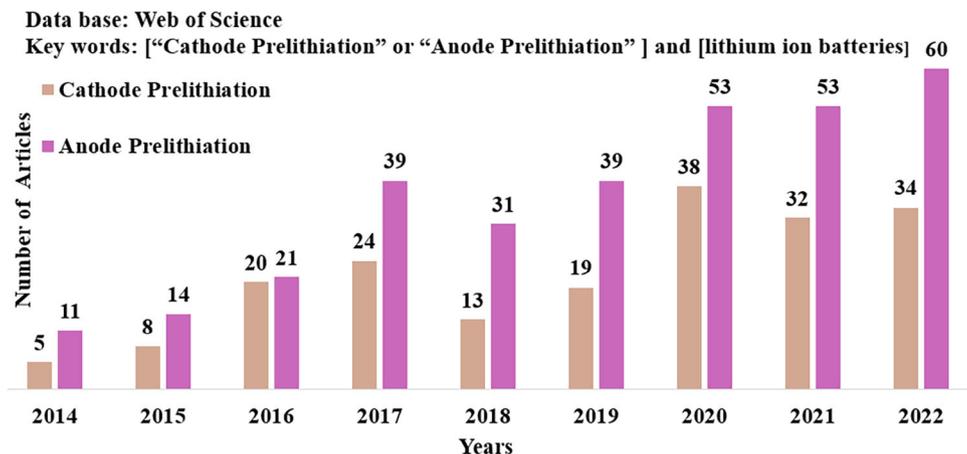


FIGURE 3 Number of papers published annually related to cathode/anode prelithiation in lithium-ion batteries, from 2014 to 2022. The search strategy was by topic: “Cathode Prelithiation” or “Anode Prelithiation” and lithium-ion batteries.

utilization of lithium metal as the counter electrode. A further complicate matter is that the additional assembly of an external cell and the removal of the prelithiation anode have to be performed before electrochemical prelithiation accomplish. Therefore, electrochemical prelithiation is limited to laboratory research and not applicable in industrial operation, due to the high cost and tedious process.

### 3.3 | Chemical prelithiation

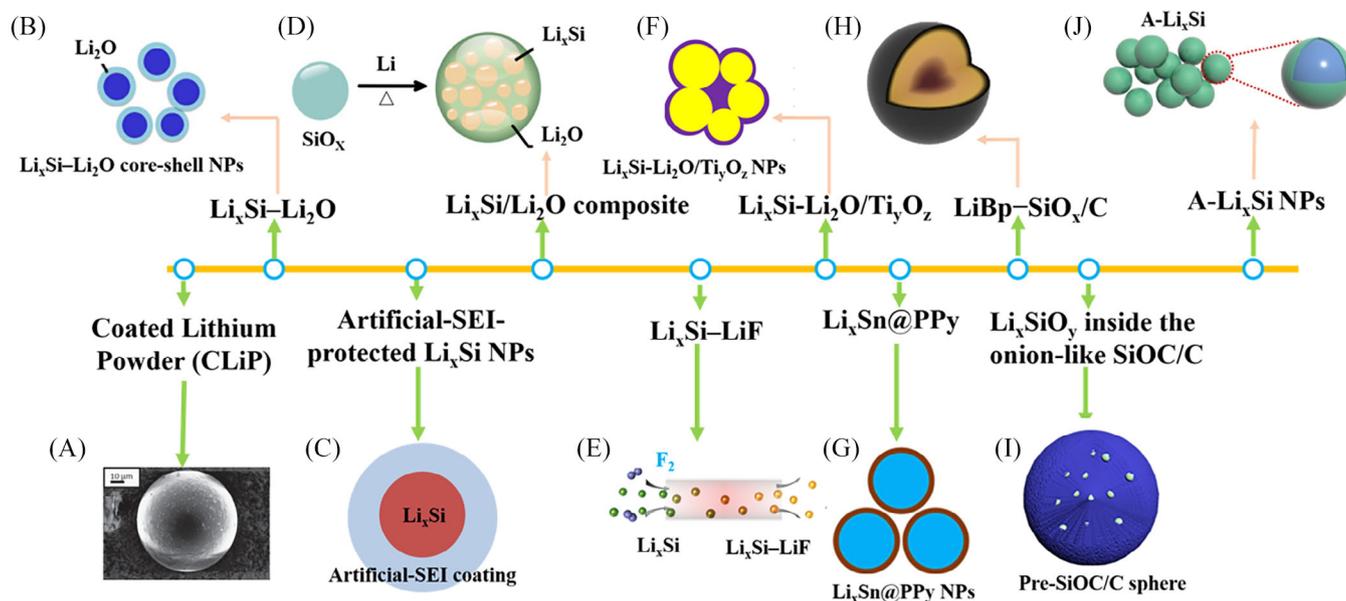
The concept of chemical prelithiation was first proposed by Obrovac et al. in 2002.<sup>72</sup> Similar to mechanical prelithiation, chemical prelithiation is driven by the potential difference between the anode material and the prelithiation agent, thus forming SEI on the anode surface (Figure 2C).<sup>73</sup> The requirement of a chemical prelithiation agent lies in the high lithium-donation capacity to provide a sufficient lithium source. As a typical chemical lithiation agent with high delithiation potential,  $\text{Li}_2\text{O}$  or  $\text{Li}_2\text{S}$  are mixed with cathode materials to supply extra lithium sources during the charging process. In contrast, lithium metal and naphthalene (Li-Naph),  $\text{Li}_x\text{Si}$  and other Li-rich alloys of low delithiation potential are directly mixed with anode materials, the lithiation process of which is milder and more efficient than mechanical prelithiation, despite certain similarity they shared.<sup>74–81</sup> Different from mechanical prelithiation and electrochemical prelithiation, chemical prelithiation matches well with the production line of state-of-art LIBs. However, broad adaptability to various and harsh environments is required for chemical prelithiation, from the perspective of low cost.

## 4 | PRELITHIATION SITE

According to where prelithiation agents are added, the prelithiation can be categorized into anode prelithiation and cathode prelithiation. Figure 3 roughly depicts the research activity of these two prelithiation locations based on the number of published papers in recent years.

### 4.1 | Anode prelithiation

Anode prelithiation, as the most intensively studied prelithiation strategy, is primarily based on mechanical electrochemical prelithiation, or chemical prelithiation types. As we mentioned above, anode prelithiation based on mechanical prelithiation or electrochemical prelithiation is limited in the practical battery manufacturing process due to the instability of metallic lithium or the tedious operation of cell assemble–dissemble, respectively.<sup>73</sup> Therefore, current research on anode prelithiation mainly focuses on chemical prelithiation. During the charging process, the active lithium source from the prelithiation agent will be first consumed to form SEI on the anode surface. In this way, the active lithium source in the cathode materials will be well preserved for the  $\text{Li}^+$  shuttle. Thus, the ideal prelithiation reagent is proposed, which has a high prelithiation capacity in the battery operating voltage range, remains stable after delithiation, and is compatible with the battery manufacturing process. As shown in Figure 4,  $\text{Li}_x\text{Si}$ , as an anode prelithiation agent, is widely and thoroughly studied.<sup>82–91</sup> Despite the high prelithiation capacity and stability in the potential window of battery operation,  $\text{Li}_x\text{Si}$  is vulnerable in practical



**FIGURE 4** Research progress of anode prelithiation agents. (A) Scanning electron microscope (SEM) 50 $\times$  magnification image of the pristine coated lithium powder. Reproduced with permission: Copyright 2014, Wiley-VCH Verlag.<sup>66</sup> (B) Schematic diagram of  $\text{Li}_x\text{Si@Li}_2\text{O}$ . Reproduced with permission: Copyright 2014, Springer Nature.<sup>83</sup> (C) Schematic diagram of the artificial SEI coating formed by reduction of 1-fluorodecane on the surface of  $\text{Li}_x\text{Si}$  NPs in cyclohexane. Reproduced with permission: Copyright 2014, American Chemical Society.<sup>82</sup> (D) Schematic diagram of  $\text{Li}_x\text{Si/Li}_2\text{O}$  composite. Reproduced with permission: Copyright 2016, National Academy of Sciences.<sup>85</sup> (E) The schematic diagram shows that  $\text{F}_2$  gas reacts with  $\text{Li}_x\text{Si}$  NP to form a uniform and compact LiF coating. Reproduced with permission: Copyright 2017, American Chemical Society.<sup>84</sup> (F) Schematic diagram of  $\text{Li}_x\text{Si-Li}_2\text{O@Ti}_y\text{O}_z$ . Reproduced with permission: Copyright 2018, American Chemical Society.<sup>88</sup> (G) Schematic diagram of  $\text{Li}_x\text{Sn@PPy}$ . Reproduced with permission: Copyright 2019, Elsevier.<sup>90</sup> (H) Schematic diagram of  $\text{LiBp-SiO}_x/\text{C}$ . Reproduced with permission: Copyright 2020, American Chemical Society.<sup>87</sup> (I) Schematic diagram of pre-SiOC/C spheres. Reproduced with permission: Copyright 2022, Elsevier.<sup>89</sup> (J) Schematic diagram of  $\text{A-Li}_x\text{Si}$  NPs. Copyright 2022 Elsevier. Reproduced with permission: Copyright 2022, Elsevier.<sup>86</sup> SEM, Scanning electron microscope.

battery manufacturing techniques due to its sensitivity to the oxygen and water in the air. Therefore, a protective layer, such as carbon,  $\text{Li}_2\text{O}$ , LiF, or other polymers, is always required to improve its compatibility with practical battery manufacturing techniques.

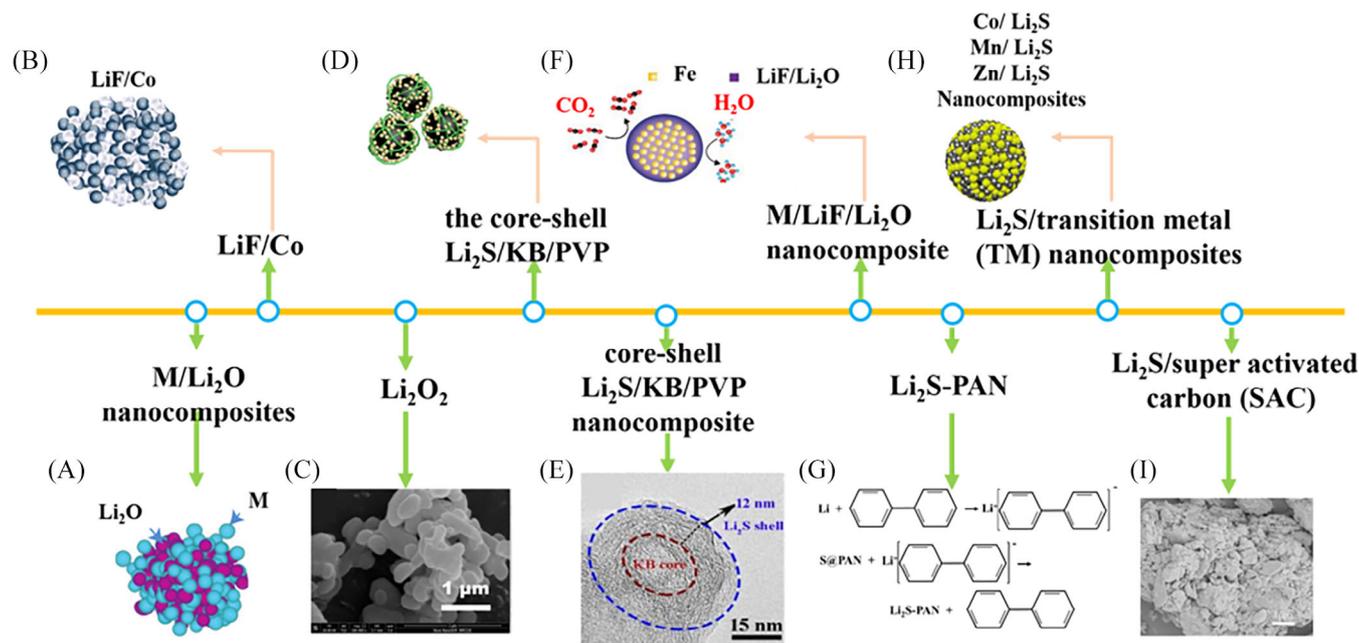
## 4.2 | Cathode prelithiation

Different from anode prelithiation, cathode prelithiation is only based on chemical prelithiation, providing an alternative and more promising prelithiation approach due to their high chemical stability, easy control of prelithiation degree, simple process, and low production costs. Cathode prelithiation agents irreversibly release active lithium ions during the first few charging process. Under the influence of the concentration gradient, lithium-ion migrates to the anode surface to form the SEI. Researchers have investigated intensively the cathode prelithiation agents in recent years, including  $\text{Li}_2\text{O}$ , LiF,  $\text{Li}_2\text{O}_2$ ,  $\text{Li}_2\text{S}$ , Li-rich layer compounds, etc. (Figure 5).<sup>92–97</sup> The delithiation potential of cathode prelithiation agents is lower than that of cathode materials, therefore SEI

formation consumes the  $\text{Li}^+$  of cathode prelithiation agents, rather than cathode materials, during the first charge process. In the discharge process, oxidized cathode material of higher redox potential holds the priority to combine with the released  $\text{Li}^+$  from the anode side, rather than oxidized prelithiation agent of lower redox potential. The above process implies an irreversible lithiation/delithiation process, leading to a sacrificial role for cathode prelithiation agents. As reported by Cui et al., the first cycle charge capacity of  $\text{LiFePO}_4/\text{graphite}$  increased by 11% when 4.8 wt%  $\text{Li}_2\text{O}/\text{Co}$  nanocomposite was added, indicating efficient active lithium compensation from LiF/Co.<sup>95</sup>

## 5 | LITHIUM SULFIDE PRELITHIATION AGENT

In Table 1, we summarize recent research with prelithiation agents for LIBs. Mainly concentrated on  $\text{Co/Li}_2\text{O}$ ,  $\text{Li}_2\text{O}_2$ ,  $\text{Li}_3\text{N}$ ,  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{S}$ -based compounds. In Figure 6, the electrochemical performance of LIBs with prelithiation agents. Among various cathode prelithiation agents,



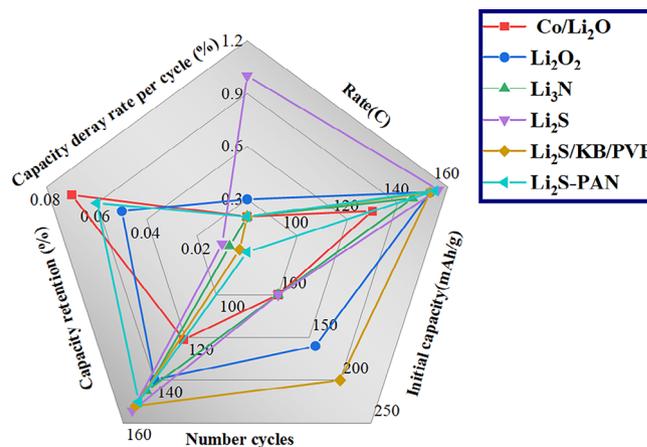
**FIGURE 5** Research progress of cathode prelithiation agents. (A) Preparation process diagram of M/Li<sub>2</sub>O composites. Reproduced with permission: Copyright 2016, Springer Nature.<sup>95</sup> (B) Schematic diagram of LiF/Co nanocomposite. Reproduced with permission: Copyright 2016, American Chemical Society.<sup>94</sup> (C) SEM images of Li<sub>2</sub>O<sub>2</sub>. Reproduced with permission: Copyright 2017, Royal Society of Chemistry.<sup>97</sup> (D) Schematic diagram of Li<sub>2</sub>S/KB/PVP. Reproduced with permission: Copyright 2017, Elsevier Ltd.<sup>47</sup> (E) High Resolution Transmission Electron Microscope (HRTEM) images of the Li<sub>2</sub>S/KB nanocomposite. Reproduced with permission: Copyright 2018, Royal Society of Chemistry.<sup>92</sup> (F) Schematic diagram of Fe/LiF/Li<sub>2</sub>O nanocomposite in the ambient air. Reproduced with permission: Copyright 2020, American Chemical Society.<sup>96</sup> (G) Synthetic reaction of Li-biphenyl and lithiation reaction of sulfurized polyacrylonitrile. Reproduced with permission: Copyright 2021, American Chemical Society.<sup>78</sup> (H) Schematic diagram of Li<sub>2</sub>S/TMs. Reproduced with permission: Copyright 2020, Wiley-Blackwell.<sup>98</sup> (I) SEM images of Li<sub>2</sub>S/super activated carbon (SAC) samples, respectively. Reproduced with permission: Copyright 2022, Springer Berlin Heidelberg.<sup>99</sup> SEM, Scanning electron microscope.

**TABLE 1** Summary of prelithiation agents for lithium-ion batteries.

Materials	Rate (C)	Initial capacity (mAh/g)	<i>n</i> th capacity (mAh/g)	Ref.
Co/Li <sub>2</sub> O	0.2	130	100th 121	95
Li <sub>2</sub> O <sub>2</sub>	0.3	153	160th 139.8	97
Li <sub>3</sub> N	0.2	146	100th 145	93
Li <sub>2</sub> S	1	156.3	100th 154.2	99
Li <sub>2</sub> S/KB/PVP	0.2	153	200th 152	92
Li <sub>2</sub> S-PAN	0.2	155	50th 150	78

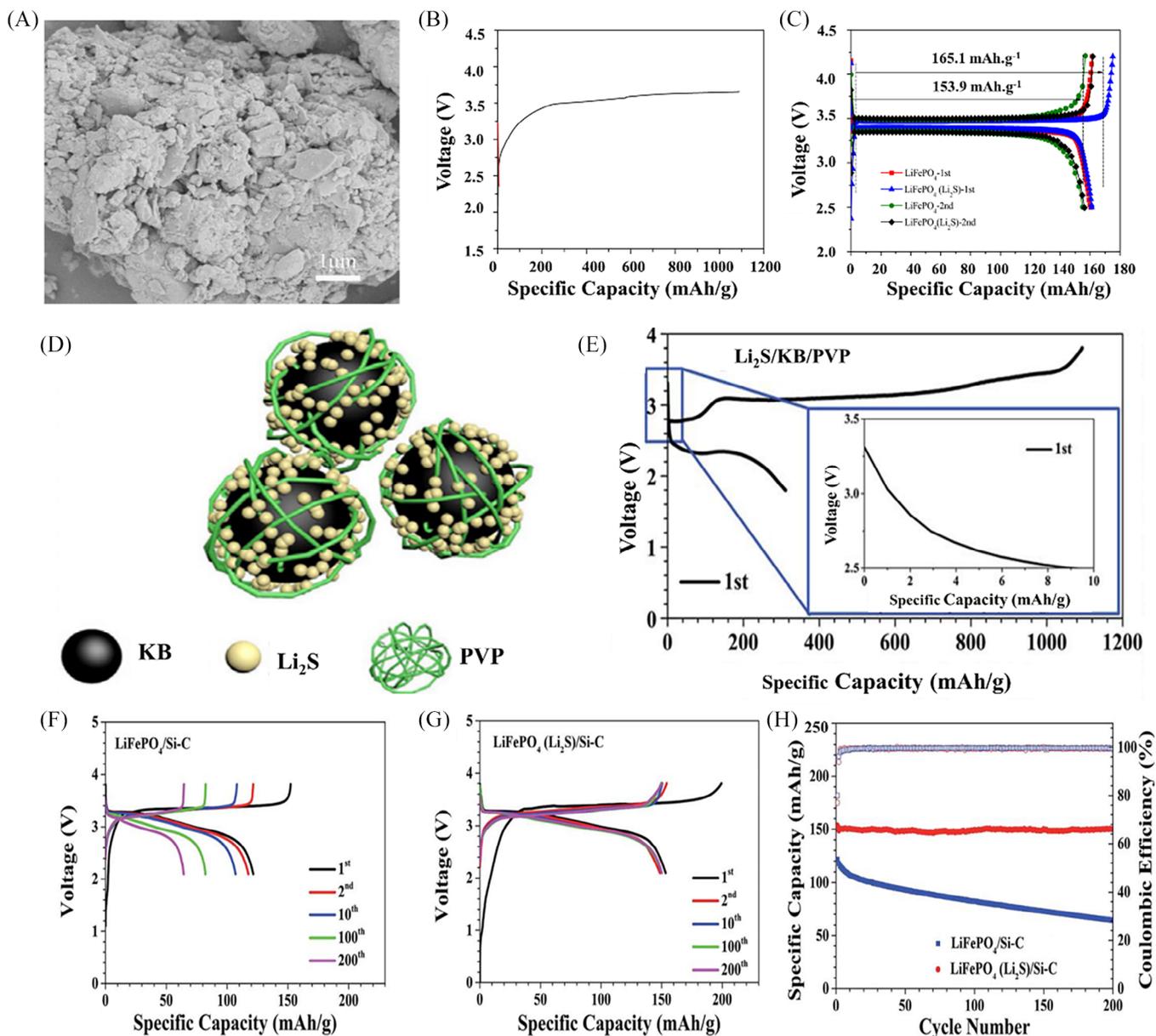
Abbreviations: KB, Ketjen black; PVP, poly(vinylpyrrolidone).

Li<sub>2</sub>S is considered a promising prelithiation agent due to its high theoretical specific capacity of 1 167 mAh/g and a suitable potential window between 2.4–3.5 V, well below the cut-off potential window of LiFePO<sub>4</sub> between 2.5–4.2 V. However, there still exist some challenges. First, high electronic resistivity and poor ionic conductivity of Li<sub>2</sub>S result in an extremely difficult Li<sup>+</sup> extraction in the first charge process and a discounted prelithiation capacity, but it is in the first charge process that SEI formation consumes extra Li<sup>+</sup>. This contradiction creates an awkward role for Li<sub>2</sub>S.



**FIGURE 6** Electrochemical performance of lithium-ion batteries with prelithiation agents.

Second, the generated polysulfides along with Li<sup>+</sup> extraction inevitably react with carbonate-based electrolytes due to the nucleophilic reaction. Such side reactions produce an undesired electron-insulating/ion-insulating layer on the cathode surface and deplete the limited electrolyte, leading to a deteriorated rate capability and fading capacity



**FIGURE 7** (A) SEM images of Li<sub>2</sub>S/SAC samples, respectively; (B) initial charge/discharge curves of the Li<sub>2</sub>S/ super activated carbon half-cell; (C) the first and second cycle charge/discharge curves of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>(Li<sub>2</sub>S) half-cells. Reproduced with permission: Copyright 2022, Springer Berlin Heidelberg.<sup>99</sup> (D) Schematic of the core-shell Li<sub>2</sub>S/KB/PVP material. Reproduced with permission: Copyright 2017, Elsevier.<sup>47</sup> (E) At 0.05 C, the voltage profile (first cycle) of the core-shell Li<sub>2</sub>S/KB/PVP half-cell was between 1.8–3.8 V; voltage profiles (1st, 2nd, 10th, 100th, and 200th cycle) of the (F) LiFePO<sub>4</sub>/Si-C and (G) LiFePO<sub>4</sub>(Li<sub>2</sub>S)/Si-C full cells; (H) discharge capacity retention and coulombic efficiency of the LiFePO<sub>4</sub>/Si-C and the LiFePO<sub>4</sub>(Li<sub>2</sub>S)/Si-C full cells. Reproduced with permission: Copyright 2018, Royal Society of Chemistry.<sup>92</sup> SEM, Scanning electron microscope.

in the long term. Third, it is very difficult to further modify Li<sub>2</sub>S, such as coating, to tackle the above problems, due to its instability with aqueous solution and low solubility in common organic solvents. Last but not least, Li<sub>2</sub>S easily reacts with moisture (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) in the air, with lithiumhydroxide (LiOH) or lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) as the product. Meantime, toxic H<sub>2</sub>S gas was also released, the high sensitivity of Li<sub>2</sub>S to the H<sub>2</sub>O/CO<sub>2</sub> in the air implies the incompatibility with the current battery

production technique. Therefore, there is an urgent need to develop air-stable Li<sub>2</sub>S prelithiation agents of high capacity and minimum side effects on the full cell.

To solve the problems of Li<sub>2</sub>S, intensive investigations have been performed. Due to high surface area and good electrical conductivity, super-activated carbon was chosen as the host to load Li<sub>2</sub>S, as reported by Ding et al.<sup>99</sup> Scanning electron microscopy (Figure 7A) showed Li<sub>2</sub>S particles of irregular shapes distributed uniformly on the

rough surface of super-activated carbon. In the electrochemical test, the as-prepared prelithiation composite shows a charge capacity of 1 087 mAh/g and a discharge capacity of 7 mAh/g in the initial cycle, indicating a high prelithiation capacity (Figure 7B). In the half-cell test, the modified LiFeO<sub>4</sub> with the above sprayed prelithiation agents delivered a charge capacity of 165.1 mAh/g, 13.9 mAh/g higher than that of pristine LiFeO<sub>4</sub> (Figure 7C). In the full cell test with graphite as anode and LiFePO<sub>4</sub> as cathode, the prelithiation agent promotes overall capacity by 11.7% at a current density of 1 C.

Another Li<sub>2</sub>S–C prelithiation agent, with Li<sub>2</sub>S as shell and Ketjen black as core (Figure 7D), was investigated by Zhan et al.<sup>47</sup> As shown in Figure 7E, Li<sub>2</sub>S/Ketjen black, in the potential range from 2.5 to 3.8 V, delivers a charge capacity of 1 093 mAh/g and a discharge capacity of only 9 mAh/g. Such irreversibility indicates a large delithiation capacity, suggesting an abundant Li<sup>+</sup> source for the SEI formation.<sup>92</sup> When the LiFePO<sub>4</sub> surface is covered with Li<sub>2</sub>S/Ketjen black, the half-cell test shows an extra voltage platform between 2.6 and 3.5 V in the initial charge process, indicating the decomposition of Li<sub>2</sub>S. As a result, LiFePO<sub>4</sub> with prelithiation agent delivers a charge capacity of 200 mAh/g, much higher than 154 mAh/g for pristine LiFePO<sub>4</sub>. What is more, no voltage platform can be identified with Li<sub>2</sub>S formation during the discharge process, indicating an irreversible delithiation process for Li<sub>2</sub>S/Ketjen black. In the full cell test, the energy density of Si–C||LiFePO<sub>4</sub> with prelithiation agent increased by 3.4%, 26.7%, 65.0%, and 110.2% for the 1st, 10th, 100th, and 200th cycles, respectively. Besides the energy density, the full cell with prelithiation agent barely shows capacity fading over 200 cycles (Figure 7F–7H). In contrast, the full cell without prelithiation agent experienced a fast capacity fading, with only 53% capacity retention after 200 cycles.

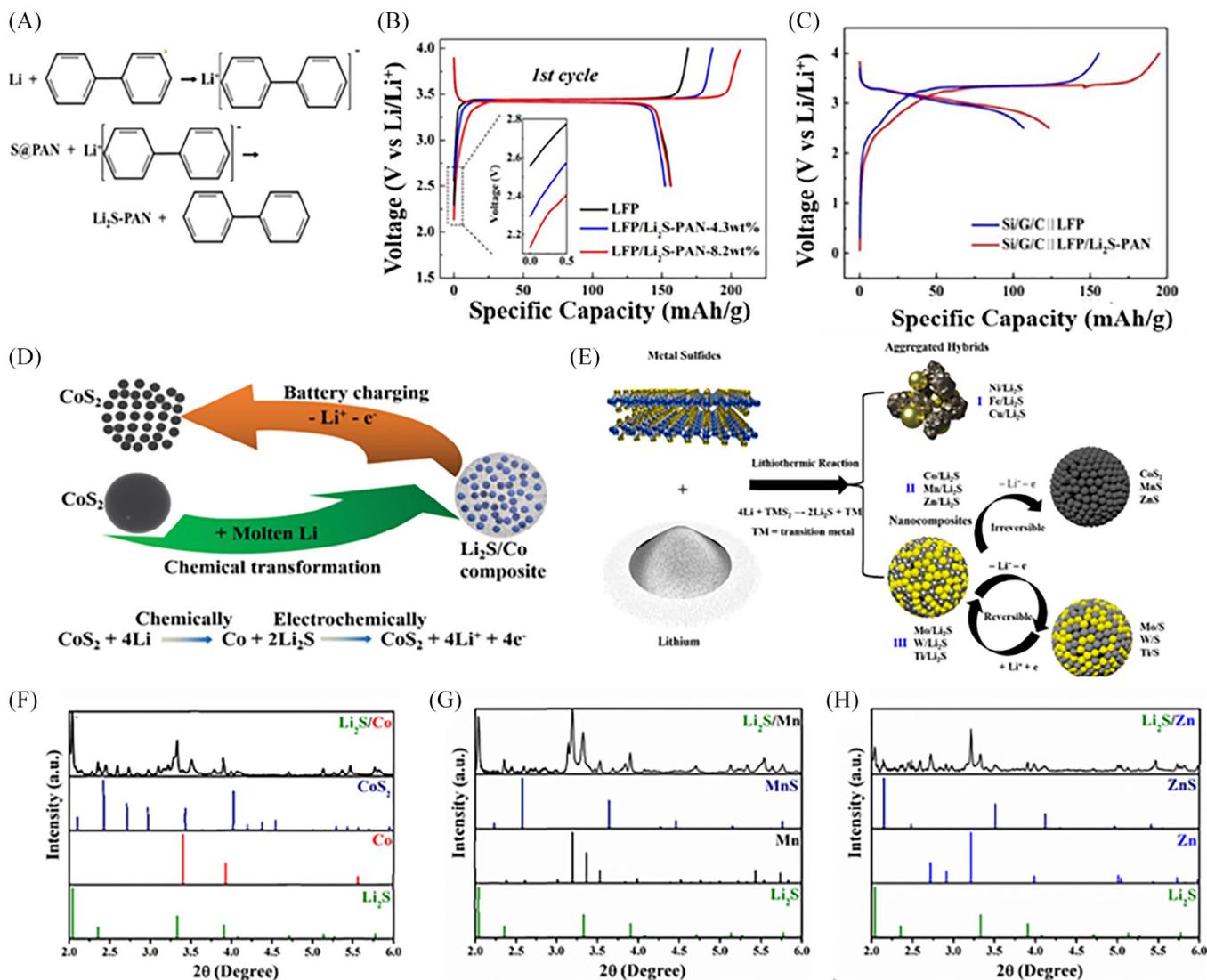
In addition to directly compositing Li<sub>2</sub>S with conductive carbon by physical mixing, the Li<sub>2</sub>S-based prelithiation composite was also prepared by the chemical method. As reported by Liu et al., Li<sub>2</sub>S–PAN was prepared by the redox reaction of sulfurized polyacrylonitrile (PAN) with Li–biphenyl complex (Figure 8A).<sup>78</sup> As shown in Figure 8B, an 8.2 wt% addition of Li<sub>2</sub>S–PAN, of high electronic conductivity and good compatibility with carbonate electrolyte, gave rise to a 22.3% capacity increase for pristine LiFePO<sub>4</sub> in the half cell. In addition, the full cell of silicon/graphite/carbon||LiFePO<sub>4</sub>/Li<sub>2</sub>S–PAN shows a reversible capacity of 123 mAh/g, 15.5% higher than that without Li<sub>2</sub>S–PAN (Figure 8C). The overall capacity improvement should be attributed to the robust SEI containing abundant LiF on the silicon anode surface, enhancing the reaction kinetics and interfacial stability. Benefitting from the compatibility between the above prelithiation process and industrial roll-to-roll electrode

preparation process, the Li<sub>2</sub>S–PAN prelithiation is valued with highly promising practical application prospects.

Beyond carbon and polymer, incorporating metal with Li<sub>2</sub>S was further investigated. As reported by Sun et al. Li<sup>+</sup> in the Li<sub>2</sub>S/Co and Li<sub>2</sub>S/Fe prelithiation agents can be completely extracted below the cathode cut-off potential in the charging process (Figure 8D).<sup>100</sup> However, there is barely any Li<sup>+</sup> recovery in the discharge process, as proved by a negligible discharge capacity of 15 mAh/g. Subsequently, Xing et al. systematically studied on how transition metals affect the Li<sub>2</sub>S electrochemical behavior.<sup>98</sup> As we know, metallothermic reduction reactions are widely used to synthesize nanocomposite due to the transient high temperature.<sup>101–103</sup> Aiding by metallothermic reduction reactions, nine transition metal/Li<sub>2</sub>S composite was synthesized, including Li<sub>2</sub>S/Ni, Li<sub>2</sub>S/Fe, Li<sub>2</sub>S/Cu, Li<sub>2</sub>S/Co, Li<sub>2</sub>S/Mn, Li<sub>2</sub>S/Zn, Li<sub>2</sub>S/Mo, Li<sub>2</sub>S/W, and Li<sub>2</sub>S/Ti (Figure 8E). The agglomeration of Ni, Cu, and Fe into metal chunks deprived Li<sub>2</sub>S/Ni, Li<sub>2</sub>S/Fe, and Li<sub>2</sub>S/Cu of the value as potential prelithiation agents. Among the other six transition metal/Li<sub>2</sub>S nanocomposites, the reversible lithiation/delithiation behaviors of Li<sub>2</sub>S/Mo, Li<sub>2</sub>S/W, and Li<sub>2</sub>S/Ti suggest cathode candidates. However, the introduction of Co, Mn, or Zn into the Li<sub>2</sub>S matrix leads to an irreversible delithiation, indicated by a charge capacity over 1 000 mAh/g and a bare discharge capacity. To study the above electrochemical process in a detailed way, high energy density X-ray diffraction (XRD) was performed. As shown in Figure 8F–8H, the XRD patterns of the products after the initial charge process were indexed to be metal sulfide. Based on the above analysis, the delithiation product of Li<sub>2</sub>S/Co, Li<sub>2</sub>S/Mn, and Li<sub>2</sub>S/Zn was in the form of metal sulfide, a more stable form than elementary sulfur, due to the hyperactively sulfophilic Co, Mn, or Zn. This unique transition guarantees the irreversibility of Li<sub>2</sub>S delithiation and maximizes the delithiation capacity, but also immobilizes the polysulfide intermediates, preventing the irreversible depletion of carbonate electrolytes. Compared with pure Li<sub>2</sub>S, Li<sub>2</sub>S/Co, Li<sub>2</sub>S/Mn, and Li<sub>2</sub>S/Zn as prelithiation agents have higher prelithiation capacities and better compatibilities with carbonate electrolytes.

## 6 | OUTLOOK

Beyond developing advanced electrode materials, electrolyte additives, binders, solvents, and separators, prelithiation agents offer another strategy to improve battery performance, aiming at higher energy density, higher initial CE, and more stable cyclability. This review paper systematically introduced the prelithiation mechanism, categorized prelithiation types, and common prelithiation



**FIGURE 8** (A) Synthetic reaction of Li-biphenyl and lithiation reaction of sulfurized polyacrylonitrile; (B) the electrochemical performance of the  $\text{LiFePO}_4$  cathode with different contents of  $\text{Li}_2\text{S-PAN/KB}$  additives for the initial cycle; (C) initial voltage profile of the Si/G/C||LFP full-cell and Si/G/C||LFP/ $\text{Li}_2\text{S-PAN}$  full cells. Reproduced with permission: Copyright 2021, American Chemical Society.<sup>78</sup> (D) Schematic of the chemical synthesis of  $\text{Li}_2\text{S/metal}$  (e.g.,  $\text{Li}_2\text{S/Co}$ ) composite and the electrochemical extraction of lithium during the battery charge process. Reproduced with permission: Copyright 2016, Wiley-VCH Verlag.<sup>100</sup> (E) Schematic diagram of  $\text{Li}_2\text{S/TMs}$  synthesis and proposed electrochemical reaction mechanism; ex situ HEXRD results of (F)  $\text{Li}_2\text{S/Co}$ , (G)  $\text{Li}_2\text{S/Mn}$ , and (H)  $\text{Li}_2\text{S/Zn}$  electrode materials after the first charge process. Reproduced with permission: Copyright 2020, Wiley-Blackwell.<sup>98</sup>

agents, and finally focused on the development of  $\text{Li}_2\text{S}$ -based prelithiation agents. Despite great achievement in recent years,  $\text{Li}_2\text{S}$ -based prelithiation agents are still facing some challenges (Figure 9), including reduced lithiation capacity due to poor electronic/ionic conductivity, high sensitivity to air, and incompatibility between polysulfide intermediate and carbonate electrolyte.

To increase the electronic/ionic conductivity, some lessons may be learned from the  $\text{Li}_2\text{S}$ -based cathode material. External carbon coating layers or transition metals have been proven effective in improving the electronic and ionic conductivity of  $\text{Li}_2\text{S}$ -based cathode material (Figure 10A). However, such strategies have not been

applied in designing  $\text{Li}_2\text{S}$ -based prelithiation agents yet. As discussed above, the external coating layer on  $\text{Li}_2\text{S}$  may facilitate electron transfer and cation diffusion, therefore improving delithiation capacity. Otherwise, prelithiation agent may be converted into dead lithium, hindering electron transfer or  $\text{Li}^+$  in turn. If further considering the high sensitivity  $\text{Li}_2\text{S}$  in the ambient environment, additional structure requirements, such as airtight and waterproof, are also necessary on the external coating layer. Otherwise, the structure of  $\text{Li}_2\text{S}$  will easily collapse by reacting with  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , generating toxic  $\text{H}_2\text{S}$  gas, and preventing it from conforming to the current production line of LIBs. Beyond improving electronic/ionic

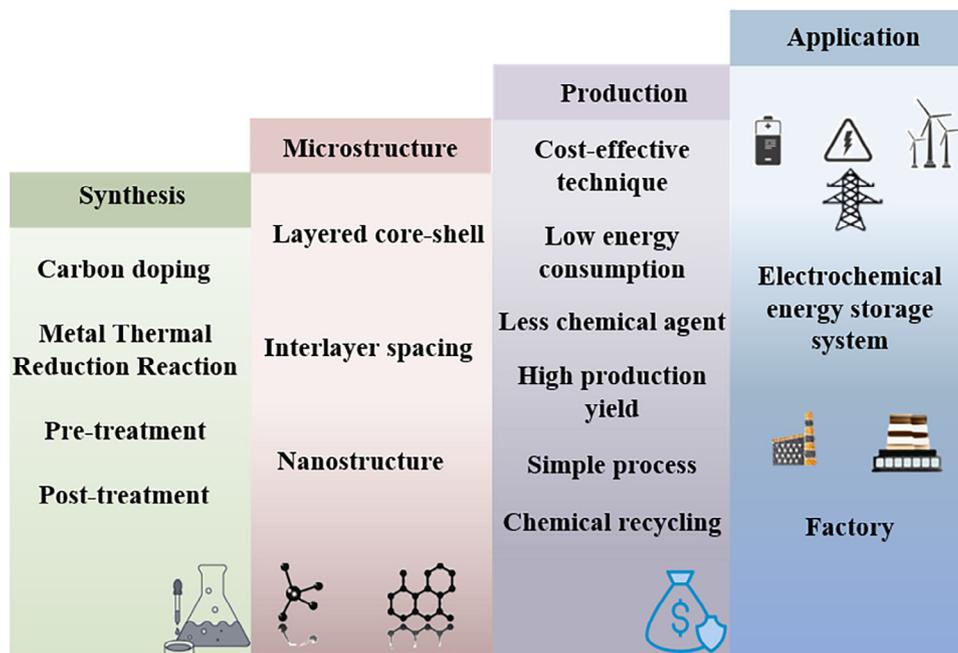


FIGURE 9 Summary of future directions and challenging perspectives of  $\text{Li}_2\text{S}$ -based cathode prelithiation materials for practical applications.

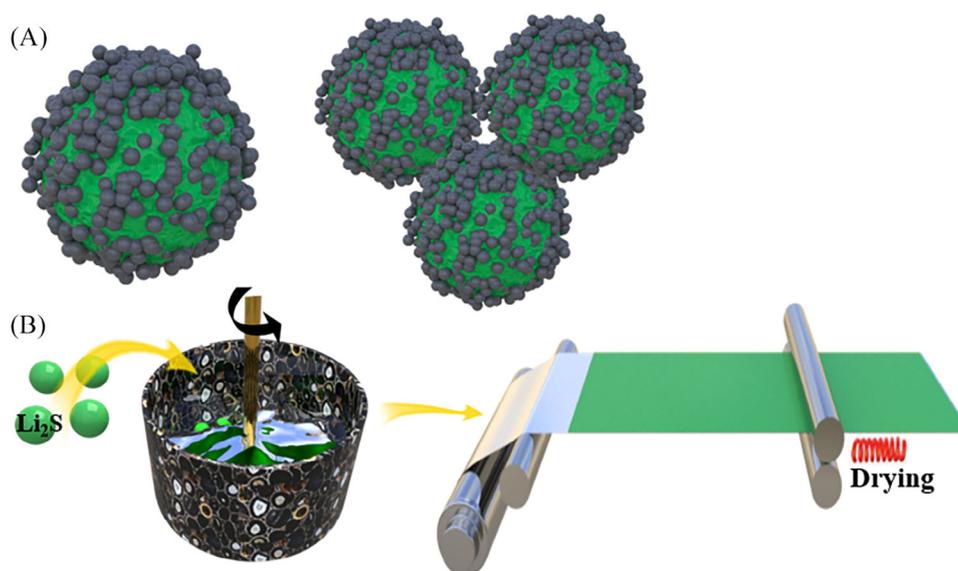


FIGURE 10 (A) Diagram of coated  $\text{Li}_2\text{S}$ . (B)  $\text{Li}_2\text{S}$  prelithiation process flowchart.

conductivity and air stability, an external coating layer with a reasonable design can also prevent polysulfide from reacting with the carbonate solvent.

Compared with compositing  $\text{Li}_2\text{S}$  with an external layer, defect engineering seems to be a more intrinsic way. According to the density functional theory calculation, removing Li atom, that is, introducing Li vacancy on the  $\text{Li}_2\text{S}$  (1 1 1) surface, results in a transition from bulk insulation to surface metallization by depleting the valence band.<sup>104</sup> In the further thermodynamics and kinetics study, it was found that positively charged Li interstitial is

more stable than negatively charged Li vacancy. From the perspective of formation energies and diffusion barriers, Li vacancy plays a more dominant role in determining  $\text{Li}_2\text{S}$  ionic conductivity.<sup>105</sup> Besides Li vacancy, the influence of S vacancy on conductivity was also studied. Based on first-principle calculations, the dynamically stable S vacancy promotes Li 2s state from the conduction band to the Fermi level and increases the overlap between the valence band and the conduction band, therefore reducing the band gap and giving rising to the transition from insulator to metal. Further analysis indicates that Li atoms pairing based on

2s–2s localized hybridization directly results in the formation of Li–Li metallic bonds, realizing the transition from insulator to metal as well.<sup>106</sup> Based on the above theoretical prediction, the introduction of either Li vacancy or S vacancy of a certain concentration will improve the conductivity of Li<sub>2</sub>S intrinsically.

Though the above proposals are promising in solving current problems for Li<sub>2</sub>S-based prelithiation agents, it should also be noted that prelithiation also gives rise to extra difficulty in battery designing, manufacturing, and recycling. Generally, prelithiation agent residuals are considered dead lithium sources with negligible effect on the battery performance (Figure 10B). However, the residuals, under thermal-runaway conditions, are highly reductive and easily bring about electrolyte decomposition. This process finally ruined the SEI and released lots of gas or heat in a short time, accelerating thermal runaway in turn. Moreover, delithiated products from prelithiation agents may react with solvent, electrolyte additive, salts, or other cell components, deteriorating battery cycling performance in the long term. Last but not least, the prelithiation technology cannot be unified for different anode materials in terms of homogeneous prelithiation, therefore a great challenge still remains in realizing an industrial prelithiation.

Overall, we hope this review could shed light on designing novel prelithiation agents not only limited to Li<sub>2</sub>S-based, but also other prelithiation agents, with desired properties including high delithiation capacity, air stability and compatibility with various electrolytes.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest. Dr. Shuhui Sun is an Associate Editor of SusMat and a coauthor of this article. To minimize bias, he was excluded from all editorial decision making related to the acceptance of this article for publication.

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