

Building Better Lithium-Sulfur Batteries—A Reassessment of the Working Mechanism

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Lithium-sulfur (Li–S) batteries have captured global attention and in-depth research interest. Nevertheless, its massive commercialization has been bothered by the “shuttle effect” caused by the soluble Li polysulfides (LiPSs) and unremitted growth of Li dendrites originated from unstable solid electrolyte interphase (SEI) film. Over the few decades have witnessed the remarkable progress of Li–S batteries, while several controversial views on the working mechanism have emerged in recent three years, which are challenging for previous related research. In this perspective, we give a brief review on the latest studies and reassess the working mechanism of Li–S batteries. With this regard, we start with a simple introduction to emphasize the significance of developing Li metal batteries. Then, we specifi-

cally elucidate the formation process and composition of SEI film. Next, we detailly discuss LiPSs cation as the dominant species in Li–S battery. Subsequently we review the case that contend no LiPSs intermediates formation in Li–S battery using γ -S as the cathode. Afterwards, we conduct a discussion between dry SEI film vs. wet SEI film on the surface of Li metal anode, followed by the strategies to design rational electrolytes for engineering stable Li metal anodes. Finally, we propose personal insights and perspectives on the development direction of Li–S batteries. We hope this timely perspective will be of great interest to the numerous scientific researchers focusing on Li–S batteries.

1. Introduction

Lithium-sulfur (Li–S) batteries have been intensively pursued as one of the most brilliant candidates for next-generation high-performance secondary batteries due to its intrinsically ultra-high theoretical energy density (2600 Wh kg^{-1}) and low-cost raw materials.^[1] However, its practical integration has long been troubled by the infamous “shuttle effect” caused by the soluble Li polysulfides (LiPSs) and unregulated growth of Li dendrites caused by unstable solid electrolyte interphase (SEI) film formed on the surface of Li metal anode. To address this dilemma, tremendous endeavors, including elaborate construction of S host materials,^[2] surface modification of Li metal anode,^[3] separator modification,^[4] electrolyte optimization,^[5,6] the introduction of interlayer,^[7] and controlling the uniaxial stack pressure during operation,^[8] have been devoted to enhancing the electrochemical performance of Li–S batteries in the past few decades. Although these strategies achieve a certain effectiveness, the aforementioned major challenges are still not completely solved, while the practical progress of Li–S batteries still remains sluggish.

In recent years, enormous efforts have been devoted to understanding the working mechanisms, including in-situ and ex-situ characterization techniques,^[9] electrochemical measurements, which, to some extent, aid researchers reveal the mystery in “black box” batteries. Furthermore, sporadic studies on the working mechanism of Li–S batteries are reported in fits and starts.^[10] Theoretically, Li–S battery is a complex system that needs to undergo a 16-electron conversion reaction. Typically, during discharge process, S_8 ring molecules are reduced into a series of LiPSs with different orders before completely transforming them into insoluble Li_2S_2/Li_2S products. It is worth noting that these LiPSs, including Li_2S_8 , Li_2S_6 and Li_2S_4 , are easily soluble in the ether-based electrolyte. It is these soluble LiPSs that are responsible for the notorious shuttle effect, which has been widely accepted as a major challenge for the development of practical Li–S batteries.^[11] In addition, solvation structure of LiPSs is frequently mentioned by Zhang’s group,^[12] some of which can indeed help to understand the properties of LiPSs, but there is no elaborate explanation on its formation process under electrolyte environment, which, in fact, is of great importance for the understanding of working mechanism for Li–S batteries.

In the most recent three years, there are several studies on working mechanism, including LiPSs cation is contended as the major species in Li–S battery system, no LiPSs intermediates form in Li–S battery using γ -S as the cathode at room temperature, and SEI film covering on the surface of Li metal anode exhibits a swelling behavior in an electrolyte environment, which pose a challenge on the previous related research. These studies seem to shine the light for the practical application of Li–S batteries. Currently, it has not yet been proven by peers. But if these results withstand further investigations, the impact on the typical implications concern-

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ing the working mechanism of Li–S batteries will be unprecedented. Although there are substantial publication summarizing the research progress, to the best of our knowledge, no attention has been paid to discuss the recent these controversial results on the working mechanism of Li–S battery.

In this perspective, we elaborately portray a schematic illustration to overview this subject: Building better Li–S batteries—A reassessment of the working mechanism, as shown in (Figure 1). Firstly, we start in section 2 to simply introduce the formation process and composition of SEI film. Then, we deeply discuss the controversy between neutral LiPSs vs. cationic LiPSs in common ether-based electrolyte and propose some thought-provoking issues. Next, we revisit the research that there is no polysulfides in the new Li–S battery system using stable γ -S at room temperature as the cathode and put forward to some insightful ideas. Subsequently, we argue the contrary of wet and dry SEI films. Afterwards, we summarize some strategies by optimizing electrolytes to construct stable Li metal anodes. Finally, we propose some personal perspectives on the development of Li–S batteries. We envision that this manuscript can find more readers for building better Li–S batteries.

2. The Formation Process and Composition of SEI Film

In recent years, considerable endeavors have been devoted to investigating the formation process and chemical composition of SEI film. Although there are some controversies, several mechanisms are proposed and widely accepted. The first one proposed by Peled is that the surface chemical reaction is stepwise and preferential reduction of specific electrolyte components.^[13] The second one is the multilayer model proposed by Kanamura et al.^[14] The third one is the Coulombic interaction mechanism proposed by Ein-Eli.^[15]



Figure 1. The overview of this perspective on “Building better Li–S batteries—A reassessment of the working mechanism”.

As we all know, the electrolyte used in rechargeable lithium-metal batteries (RLMBs) generally contains organic solvents and Li salts. Owing to the high reactivity, Li metal can immediately react with almost all electrolyte upon contact to form a layer of passivating film covering on the surface of Li metal anode, which is mainly composed of Li_2CO_3 , Li_2O , and LiOH species.^[16] When fluorinated electrolytes are used, LiF-rich SEI film can be formed. It is worthy to note that the chemical composition and spatial distribution of SEI film is strongly dependent on the electrolyte formulation^[13,17,18] and operation temperature.^[19]

3. Neutral LiPSs versus Cationic LiPSs

From the perspective of working principle, neutral Li polysulfides (LiPSs) have long been embraced as the main species in electrolyte of Li–S battery, which play a decisive role in electrochemical performance of batteries. However, a recent pioneering finding challenges this viewpoint. Writing in the latest issue of *Chem* in August 2022, Song et al.^[20] confirmed that cationic LiPSs is the main species in Li–S battery electrolyte.

To better understand the difference between neutral LiPSs and cationic LiPSs, we have also presented an optimized structure based on density functional theory (DFT) calculations (Figure 2a). In fact, the research around the reaction mechanism of Li–S battery have never been stopped. The past few decades have witnessed the impressive findings in the field of Li–S batteries. For instance, S_4^{2-} is regarded as the dominant reaction intermediate in common ether-based electrolyte by using operando UV-vis spectroscopy.^[21] Other research groups have recruited various in-situ characterization techniques to monitor the main species in Li–S battery system, such as nuclear magnetic resonance (NMR) ($\text{S}_2^{\bullet-}$ and $\text{S}_3^{\bullet-}$ radicals were predicted),^[22] electron paramagnetic resonance (EPR) (monitoring the formation and evolution of $\text{S}_3^{\bullet-}$ free radical),^[23] X-ray diffraction (XRD) (directly observing neutral LiPSs),^[24] and X-ray absorption near-edge spectroscopy (XANES) (S^{2-} is the primary species during discharge process),^[25] which both greatly promote the understanding on underlying reaction mechanism of Li–S battery. However, the existing form of LiPSs in electrolyte still remains poorly understood.

As a striking example, published in *Chem*, Song et al.^[20] from Tsinghua University examine this question. Combining electron spray ionization mass spectrometry (ESI-MS), ^7Li NMR spectroscopy with molecular dynamics (MD) simulation, the authors confirmed the existence of LiPSs cation in Li–S battery electrolyte. Compared with neutral LiPSs, LiPSs cations tend to be repulsed when close to the side of cathode, and are easier to be absorbed to the surface of Li metal anode owing to electrostatic attraction (Figure 2b). Furthermore, the researchers contend that cationic LiPSs are unfavorable to the conversion reaction by means of experimental results and theoretical calculations. To address this dilemma, they prepare a low concentration bistrifluoromethanesulfonimide lithium salt (LiTFSI) ether-based electrolyte to suppress the formation of LiPSs

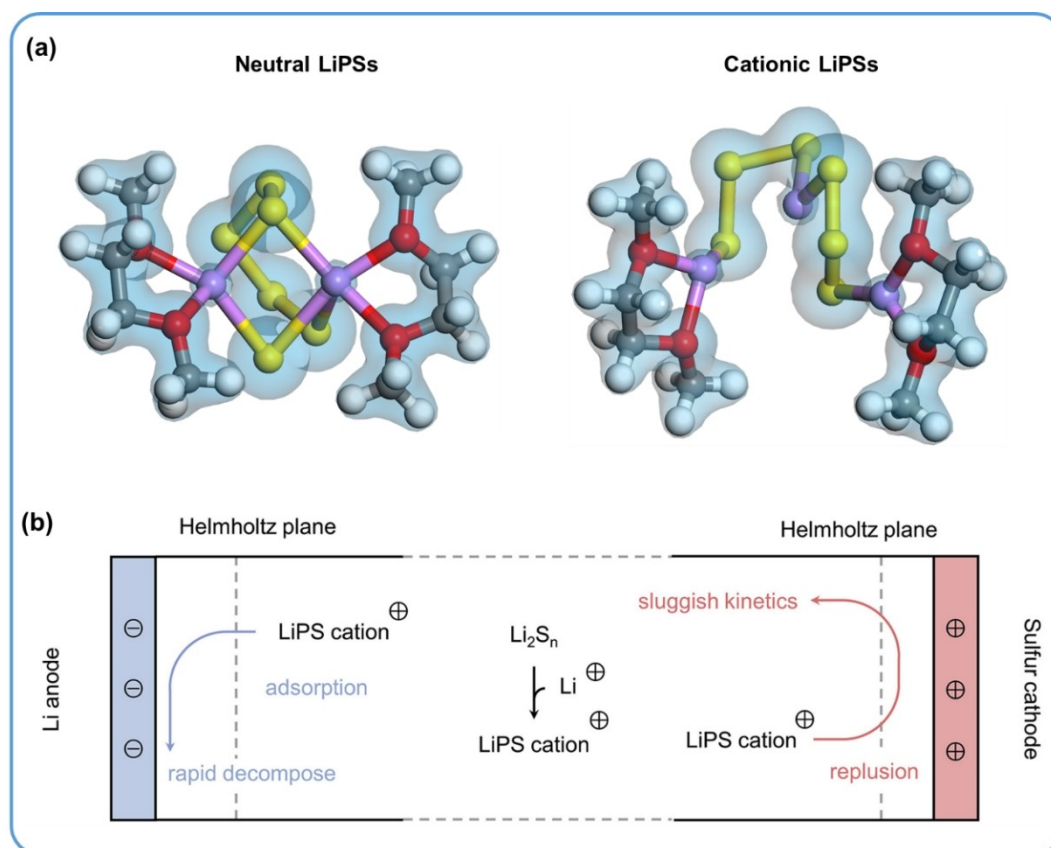


Figure 2. Schematic illustration of neutral LiPSs and cationic LiPSs and kinetic evaluation on LiPSs cation in electrolyte of Li-S battery. a) The existence form of neutral LiPSs and cationic LiPSs. b) The interaction between cationic LiPSs and electric double layer at S cathode and Li metal anode. Reproduced from Ref. [20]. Copyright (2022) with permission from Elsevier.

cation, thus effectively improving the electrochemical performance of Li-S pouch cells. Admittedly, this standpoint runs counter to that of high concentrated electrolytes, which can effectively inhibit the shuttle effect caused by soluble LiPSs owing to the lack of free solvent.^[26] This innovation that break tradition is not yet confirmed. But if other Li salts are still applicable, the impact on the working mechanism of Li-S battery will be of great significance.

In addition, we notice that considerable amounts of excellent research has been devoted to suppressing the shuttle effect of neutral LiPSs by using adsorption strategy in the past few decades.^[27] It is worth noting that the adsorption strategy generally include the design of polar S host materials, which has been considered as a prospective avenue for the shuttle behavior of neutral LiPSs. Obviously, the perspective of this work is contradictory with those design of positively charged polar materials that can effectively adsorb the neutral LiPSs. We cannot make sweeping statement if these strategies are also applicable to LiPSs cation. This work is treated as a brand-new paradigm, which will have a profound significance on the field of Li-S batteries and help tremendously in moving the field ahead.

It is worth mentioning that solvation structure of LiPSs intermediates plays an important role in the electrochemical performance of Li-S batteries. Very recently, solvation structure

of LiPSs is frequently mentioned by Zhang's group,^[12] some of which can indeed help to understand the neutral LiPSs, but there is no elaborate explanation on its formation process in electrolyte environment, which is of great importance for the understanding of Li-S batteries and worthy of further exploration in future research. Considering the sluggish kinetic of LiPSs cations in the side of cathode while aggressive with Li metal anodes, constructing thin Li metal anode with a stable SEI film and regulating the amount of Li salt or Li^+ concentration in the electrolyte are highly needed.

In short, Song et al.^[20] report impressive finding in the field of Li-S battery, but there are several issues to address before Li-S batteries can become practical applications. For instance, safety issues related to Li metal anode. The authors deserve credit for challenging the long-held axiom in Li-S battery chemistry, where neutral LiPSs governs the whole redox reaction process. Now, cationic LiPSs is considered as an enabler of electrochemical performance of Li-S battery. The importance of the LiPSs for battery electrochemical performance justifies the efforts, and in-situ characterization techniques are still expected to hopefully motivate further understanding on the reaction mechanism of Li-S battery.

4. No LiPSs

LiPSs generated during cycling process have long been recognized to play a decisive role in electrochemical performance of Li–S batteries in ether-based electrolyte. However, recently, an intriguing direct reversible redox mechanism between stable γ -S and Li_2S at room temperature in ester-based electrolyte instead of forming LiPSs is proposed.

It is worth mentioning that solvation structure of LiPSs intermediates play a key role in the Li–S batteries, and their existing form is strongly related with the electrochemical performance of practical Li–S batteries. It is worth mentioning that solvation structure of LiPSs plays an important role in the electrochemical performance of Li–S batteries. Very recently, solvation structure of LiPSs is frequently mentioned by Zhang's group,^[12] some of which can indeed help to understand the neutral LiPSs, but there is no elaborate explanation on its formation process in electrolyte environment, which is of great importance for the understanding of Li–S batteries and worthy of further exploration in future research.

As is well-known, rechargeable lithium-ion batteries (RLIBs) can achieve ultralong cycling lifetime, which should be attributed to unique working mechanism. More precisely, Li^+ ions migrate back and forth between the cathode and the anode under operation while electrode materials without deformation. This working mechanism is vividly nicknamed as "rock-chair".^[28] Differently, Li–S battery is a complicated system,

which needs to undergo a 16-electrons conversion reaction, meaning that the morphology of cathode and anode materials can change during cycling process. What is worse, the shuttle effect of soluble LiPSs worsens the operation environment of Li–S batteries, making the system more complicated. These factors should be in charge of the poor cycling lifetime of Li–S batteries. Is there any strategy to avoid the formation of LiPSs and prolong the cycling lifetime of Li–S battery?

Recently in *Communications Chemistry*, Vibha Kalra and colleagues^[29] response this question and get out of the aforementioned dilemma. They found that there is a direct reversible phase transformation between stable γ -monoclinic S and Li_2S at room temperature without the formation of LiPSs in ester-based electrolyte (Figure 3a), which is completely different from previously reported publications. As a striking comparison, in conventional Li–S battery, α -S as the cathode active material is stable in the form of S_8 molecule, which needs to undergo a conversion reaction "from solid to liquid to solid" with the formation of intermediate LiPSs, thus playing a pivotal role in electrochemical performance of Li–S batteries in ether-based electrolyte (Figure 3b). It is worth noting that Li–S battery using this stable γ -S exhibits impressive cycling lifetime (4000 cycles) in ester-based electrolyte. In addition to this report, we notice that there have been several studies avoiding the LiPSs formation to build better Li–S battery by using smaller S (α -S) molecules.^[30] It is worth noting that the two excellent studies both mentioned nanoconfined method, which

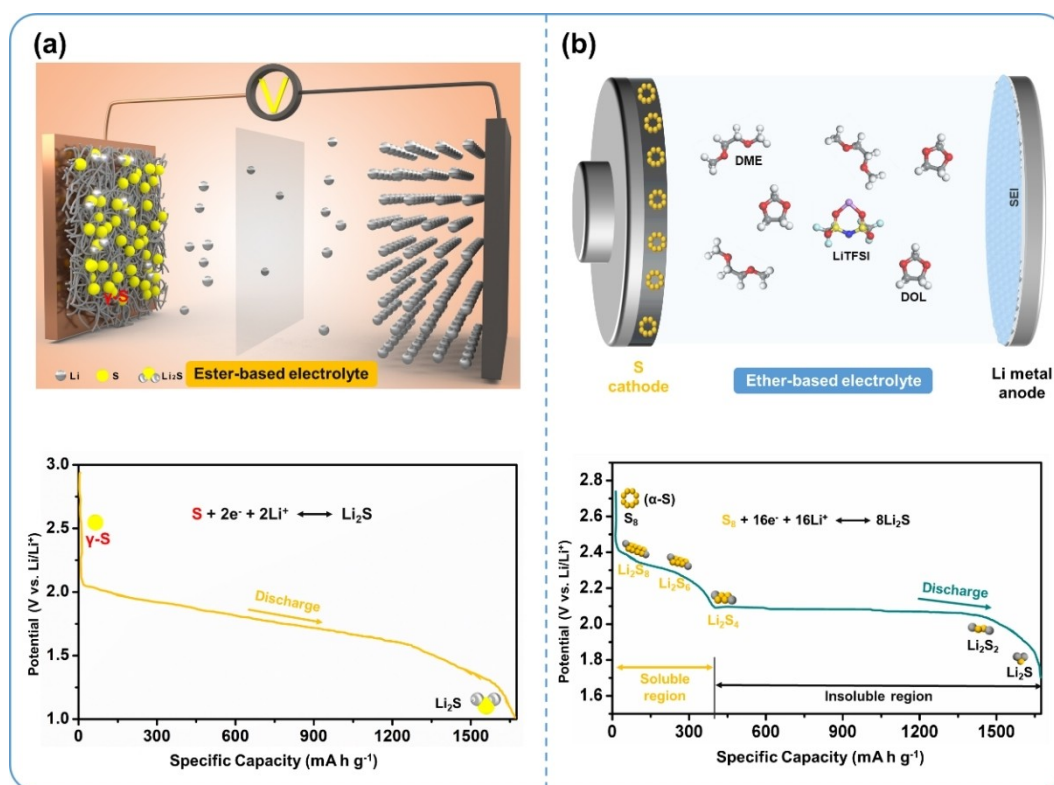


Figure 3. The comparison of the reaction mechanism of S with different crystal structures for Li–S batteries. a) Schematic diagram of a direct conversion between stable γ -S and Li_2S without the formation of intermediate LiPSs in ester-based electrolyte. b) Schematic diagram of a conversion reaction between α -S and Li_2S with the formation of intermediate LiPSs in ether-based electrolyte.

can confine small S molecules in a microporous carbon matrix, thus avoiding the LiPSs formation in Li–S battery.

Although the researchers have conducted the basic electrochemical tests and ex-situ characterization measurements on cycled batteries to elucidate the redox mechanism, it does not seem convincing enough. In-situ/operando characterization techniques have long been accepted as powerful tools to reveal the reaction mechanism in Li–S batteries.^[31] Therefore, it is considerably desirable to recruit these characterization methods for providing more convincing evidence. In the past few decades, researchers have accumulated a wealth of experience and knowledge on carbonate-based electrolytes^[32] and in-situ/operando characterization techniques in the field of LIBs, which can be hopefully transplanted to the research of Li–S batteries. If the reaction mechanism proposed by Pai and coworkers^[29] can be proven by subsequent studies through in-situ/operando characterization techniques, the major challenge of Li–S batteries would be only focused on Li metal anode. The next thing to do is to design rational Li metal anode with stable protective film, which highly needs a seamless cooperation between academia and industry. In this case, the practical application of Li–S batteries will be greatly promoted. On the other hand, the sluggish solid-solid conversion reaction may limit the application of Li–S batteries from particular scenarios, for instance, fast charging/discharging.

In short, Pai and co-authors reported a striking discovery in the field of Li–S battery that a direct reversible redox between stable γ -S to Li_2S at room temperature occurs rather than forming the LiPSs, which breaks the conventional recognition and updates the fundamental understanding of Li–S battery. This is an unexpected discovery that may make large-scale use of lithium-sulfur batteries possible. Frankly speaking, the authors deserve credit for proposing completely different reaction mechanism, but practical challenges have to be overcome. For instance, the cost of γ -S cathode mass production and safety risks related to Li metal anode needs to be paid special attention. Despite these challenges, the reaction mechanism reported by Pai and colleagues provide a brand-new perspective in the field of Li–S battery. Currently, we cannot arbitrarily conclude whether the reaction mechanism proposed by Pai et al.^[29] is correct, but at least, this work is fueling in further understanding on new fundamental research of Li–S battery.

5. Dry SEI film vs. Wet SEI film

Solid electrolyte interphase (SEI) has long been recognized to prevent the electrolyte from further being decomposed and depleted during the subsequent cycles; however, the latest studies challenge the conventional cognition, and researchers contend that the electrolyte can enter SEI film.

In order to promote the practical applications of LMBs, the majority of laboratory research has been carried out with coin cells using thick Li metal plates, which are frequently reported as a paradigm of fundamental research and used to predict the cycle lifetime of LMBs.^[33] Therefore, for a long time, a thick Li

metal anode has been accepted to have a longer cycle lifetime. However, recently, writing in *Nature Energy*, Niu and co-authors^[34] challenged this long-held viewpoint, and confirmed that a thin-Li metal anode can realize a longer cycle lifetime in practical Li metal pouch cell compared with the thick Li metal anode. It is worth noting that the researchers creatively proposed the concept of “dry SEI” film to elucidate the degradation mechanism of practical 350 Wh kg^{−1} Li pouch cell using a thin Li metal anode. As mentioned in the article, the researchers stated that “dry SEI” film does not transport Li^+ owing to the lack of electrolyte. On the contrary, “wet SEI film” plays a decisive role in the transport of Li^+ (Figure 4a). Based on this understanding, the researchers appeal that a thin and uniform “wet SEI film” is highly desirable for the design of high-energy LMBs. Compared with pouch cell, lab-assembled coin cells have a flooded electrolyte, so that generated SEI film on the surface of Li metal anode usually remains wetted state, which has recently been confirmed by Cui and colleagues^[35] in *Science*. The authors confirmed that there is an obvious swelling of the SEI film on the surface of Li metal anode by electrochemical experiments and advanced characterization techniques (Figure 4b).

As we all know, SEI film has long been recognized to simultaneously possess the properties of ionically conductive and electronically insulating, which can prevent the electrolyte from being further decomposed. According to the perspective proposed by Cui and colleagues, swelling behavior of SEI film indicates that solvent molecules are able to enter the SEI film, which subverts the conventional recognition that SEI film allows only bare Li^+ to pass through but prevent solvent molecules.^[36,37] Unambiguously, this work sweeps the previous statement that electrolyte cannot enter the SEI film due to the existence of compact inner SEI film (Figure 4c)^[38] and Li^+ have to undergo desolvation step before through the SEI film (Figure 4d).^[36] Based on the research findings reported by Cui and colleagues, subsequent researchers might need to reexamine the role of SEI film, the desolvation process and transport mechanism of Li^+ in the SEI film. Theoretically, organic components, like polymeric species, will be certainly swellable. Considering the porosity of organic polymer and size of solvent molecules, it is easy to understand the swelling behavior of SEI film. It is worth noting that numerous studies have revealed that the composition of SEI film is strongly dependent on the electrolyte composition^[13,17,18] and operation temperature.^[19]

From the two classical cases highlighted in this section,^[34,35] we notice that a common feature that electrolyte can enter the SEI film in the latest studies, which update the fundamental cognition on SEI film. It is worthy of to note that the standpoint on the stabilizing effect of the SEI film have been challenged as early as in 2018, when Ming et al. argued that solvation structure of Li^+ is more important than SEI film (Figure 4e).^[39] In Li–S battery system, controlling the amount of electrolyte used in Li–S battery is the key to realize a wet SEI film and suppress the shuttle effect of LiPSs. Currently, we cannot arbitrarily assert that these excellent works are the final breakthrough of SEI

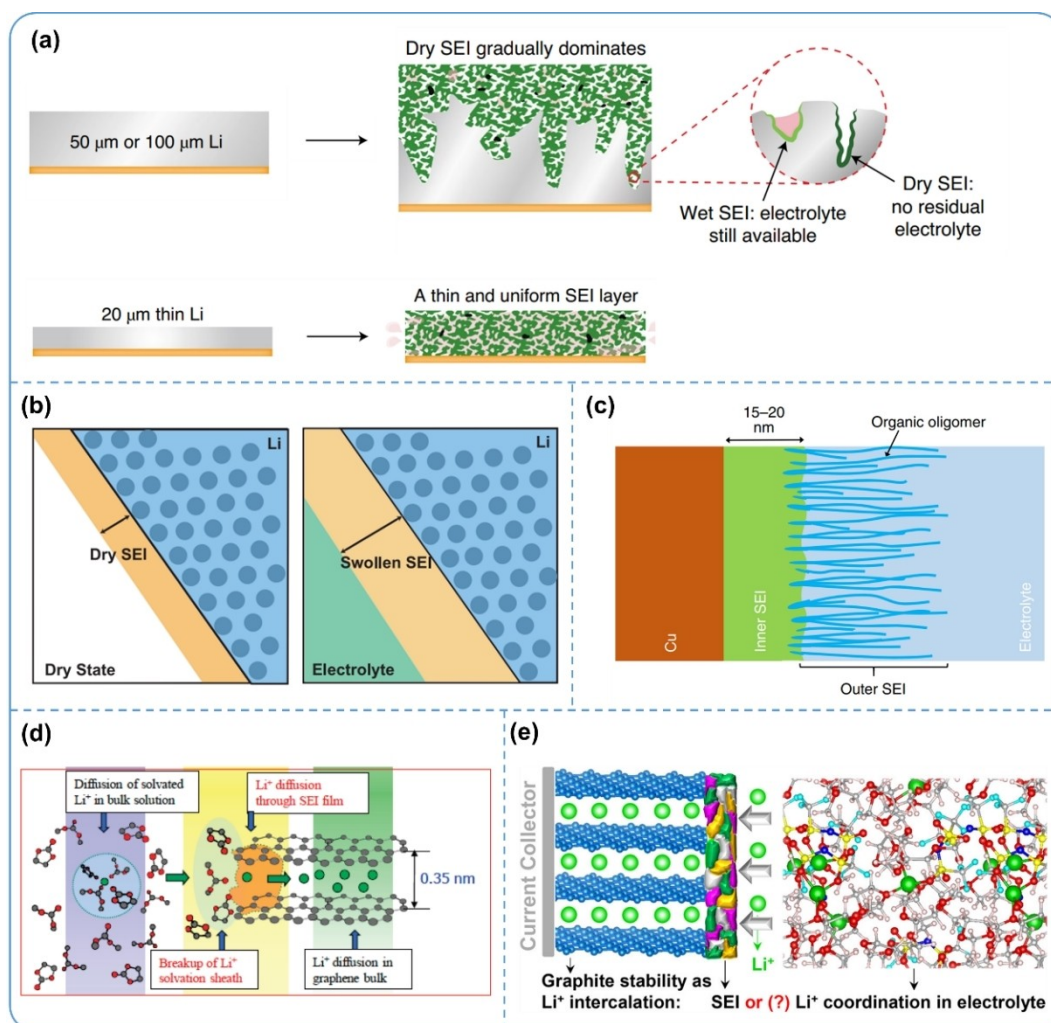


Figure 4. The schematic diagram of SEI film and charging process. a) A comparison of wet SEI film and dry SEI film. Reproduced with permission from Ref. [34]. Copyright (2019) Nature Group Publishing. b) A comparison of dry SEI and swollen SEI. Reproduced with permission from Ref. [35]. Copyright (2022) AAAS. c) The schematic diagram of an SEI model. The inner SEI film is dense and impermeable to electrolytes. The loose and porous organic oligomer is permeable to electrolytes. Reproduced with permission from Ref. [38]. Copyright (2020) Nature Group Publishing. d) The schematic illustration of desolvation process of a solvated Li^+ during charging process. Reproduced with permission from Ref. [36]. Copyright (2010) American Chemical Society. e) Schematic illustration of the controversy on the solvation structure of Li^+ and SEI film in a LIB using graphite as an anode. Reproduced with permission from Ref. [39]. Copyright (2018) American Chemical Society.

film, but it is certain that these pioneering studies are fueling in the fundamental understanding of SEI film.

6. Optimizing Electrolytes to Construct Stable SEI Film

Undoubtedly, electrolyte plays a critical role in the stable operation of RLMBs. Therefore, optimizing electrolyte recipes is of imperative significance for elevating the electrochemical performance of Li–S batteries.

It seems that designing functional electrolytes from molecular level can cater Li metal anode by tailoring a stable SEI film in situ to passive Li metal metals.^[40] Very recently, some studies have provided us with some ideas that developing electrolytes, especially the design of fluorinated electrolytes from the

molecular level could tailor a stable SEI film on the surface of Li metal anode.^[6,18,40] Although fluorinated electrolytes have gained popularity in recent years, highly fluorinated or perfluorinated solvents are not necessarily desirable. Very recently, Yu et al.^[42] discovered that the degree of fluorination needs to be finely tuned, and partially fluorinated electrolyte has a better effect on optimizing the electrochemical performance of RLMBs. Combining the experimental results reported by Song et al.,^[20] exploring partially fluorinated diluted electrolytes might a promising solution for building better Li–S batteries.

7. Conclusions and Perspectives

In conclusion, we have revisited the latest studies on RLMBs, which can be treated as the significant milestone of recharge-

able RLMBs. Some may navigate the practical applications of Li–S batteries. Currently, we cannot draw conclusion which viewpoints are right referred in this perspective, but at least, these findings are valuable and are fueling in further understanding on the reaction mechanism of Li–S battery.

Optimizing the components in the Li–S battery and combining them. Some standpoints referred in this contribution seem rational, but from the perspective of practical applications, more endeavors should be allotted to admirable studies, and then combine them together optimally, as any short slabs might give rise to the collapse of the commercialization blueprint of Li–S batteries.^[43] This mainly because Li–S battery is a whole that demands every component work together. More directly, if the Li metal anode used in RLMBs exists these defects or does not form stable SEI film, no matter how researchers optimize the cathode modification, the separator modification or the electrolyte recipes are both futile, which is because battery will become undoubtedly terrible starting from the first cycle. If these results can be validated by peers, we envision that the structure of a better Li–S battery should be featured by: thin Li metal foil as the anode with a wetted SEI film paired with γ -S as the cathode or α -S as the cathode using suitable diluted electrolytes.

In addition to Li metal anodes, S cathodes, the others should be also considered, including the rational design of electrolytes, separators, current collectors, binders, and conductive additive. This is because the introduction of current collectors, binders, conductive additives can greatly lower the energy density of Li–S battery when preparing S cathodes. In pursuit of high energy density of Li–S batteries, developing freestanding S cathodes with high mass loading is highly desirable in future research. If the working mechanism of Li–S battery using γ -S as the cathode is proven to be right by subsequent researchers, extensive efforts on large-scale preparation of γ -S are highly desirable. If γ -S can be prepared on a large scale, dry compressibility of holey graphene might provide some idea for constructing high mass loading S cathode.^[44] Only the mass loading reaches a certain value can the energy density of Li–S battery surpass that of the current commercial RLMBs.

Developing more advanced characterization techniques to further confirm the working mechanism of Li–S battery using γ -S. In order to better understand the key step during battery operation, it is highly needed to employ in-situ/operando characterization techniques for tracking the whole charge process, which seems a grand challenge, but from another perspective, it is exactly an opportunity. In recent years, some of the in-situ/operando characterization tools have been frequently recruited to understand the detailed reaction mechanism, providing many valuable guidelines for the building better Li–S batteries.

If the dilemma facing Li–S batteries can be thoroughly overcome, the massive commercialization is no longer a pipe-dream. A breakthrough for Li–S batteries might be more imminent than ever, which will certainly motivate further activities for the commercialization of this type of battery.

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Conflict of Interest

The authors declare no competing interests.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: γ -S · cationic LIPSS · Li–S batteries · wet SEI film · working mechanism

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