Research
Green Chemical Engineering—Review

Recent Advances in Energy Chemical Engineering of Next-Generation Lithium Batteries

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A B S T R A C T

Rechargeable lithium-ion batteries (LIBs) afford a profound impact on our modern daily life. However, LIBs are approaching the theoretical energy density, due to the inherent limitations of intercalation chemistry; thus, they cannot further satisfy the increasing demands of portable electronics, electric vehicles, and grids. Therefore, battery chemistries beyond LIBs are being widely investigated. Next-generation lithium (Li) batteries, which employ Li metal as the anode and intercalation or conversion materials as the cathode, receive the most intensive interest due to their high energy density and excellent potential for commercialization. Moreover, significant progress has been achieved in Li batteries attributed to the increasing fundamental understanding of the materials and reactions, as well as to technological improvement. This review starts by summarizing the electrolytes for next-generation Li batteries. Key challenges and recent progress in lithium-ion, lithium–sulfur, and lithium–oxygen batteries are then reviewed from the perspective of energy and chemical engineering science. Finally, possible directions for further development in Li batteries are presented. Next-generation Li batteries are expected to promote the sustainable development of human civilization.

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1. Introduction

Since commercial lithium-ion batteries (LIBs) were first released by Sony Corporation in 1991 [1], they have become essential energy storage devices that profoundly affect our daily life. In particular, LIBs currently dominate the market in powering portable electronics and electric vehicles. The energy density of LIBs at cell level has reached 260 W·h·kg^{-1} and 700 W·h·L^{-1} after rapid growth over the past 27 years [2,3]. In order to further sustain the rapid development of portable electronics, electric vehicles, and grid-scale energy storage, batteries with a higher energy density are eagerly anticipated. However, the energy density of LIBs is approaching the theoretical value, due to the inherent limitations of intercalation chemistry [4,5]. Thus, it is difficult to achieve a breakthrough with improvements in current LIB processing technology. Therefore, emerging solutions are highly required.

To circumvent the bottleneck of intercalation chemistry in LIBs, innovations in battery chemistry and the energy chemical

engineering to scale up the energy storage process is strongly requested [6–10]. The intercalation chemistry of LIBs is based on the single-electron reaction, in which lithium (Li) ions shuttle back and forth between the anode and cathode during the electrochemical redox reaction [11]. Both the anode and cathode are highly reversible and have minimal changes in their crystal structures during intercalation and de-intercalation. Intercalation anodes, such as graphite, exhibit specific capacities of 372 mA·h·g^{-1} [12]. Intercalation cathodes, such as layered $LiCoO_2$ (LCO), spinel $LiMn_2O_4$ (LMO), layered $LiNi_xMn_yCo_zO_2$ (NMC) with different stoichiometries, layered $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), and olivine $LiFePO_4$ (LFP), demonstrate specific capacities of up to about 250 mA·h·g^{-1} [11–13]. In general, the energy density of a battery can be estimated by the specific capacity of the electrodes and the working voltage of the battery. Hence, the limited specific capacity of intercalation electrodes prevents the increase in energy density of LIBs.

Unlike intercalation electrodes, conversion anodes and cathodes break and create chemical bonds during the insertion and extraction of Li ions. This process corresponds to the transfer of more than one electron when 1 mol of discharge product forms, and delivers higher specific capacity and energy density than the use of intercalation electrodes [14]. Conversion anodes, such as Li, have

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specific capacities around 10 times greater than that of a graphite anode. Conversion cathodes, such as sulfur (S) and oxygen (O_2), have specific capacities greater than 1600 mA·h·g^{-1} [15]. Employing conversion electrodes in a rechargeable battery system significantly improves the energy density. For example, the theoretical energy densities of Li–S and Li–O_2 batteries can reach 2600 and 3500 W·h·kg^{-1}, respectively, which far exceed that of the current LIBs [15].

In fact, the application of conversion electrodes in rechargeable battery systems is not a new idea, as it first appeared before the emergency of intercalation electrodes. However, the inherent problems of conversion electrodes, such as short lifespan and severe safety concerns caused by large volume fluctuations and poor reversibility of electrode reactions, greatly hinder their practical application [14,16]. Nevertheless, tremendous practical progress has been made in practical conversion electrodes, which has greatly benefited from continual improvements in nanotechnology, computational simulations, and advanced characterization technologies, especially during the last two decades.

Among the various battery chemistries being investigated as possible next-generation batteries, Li batteries, which employ Li metal as the anode and conversion or intercalation materials as the cathode, have become a topic of particular interest (Fig. 1) because of the extremely high theoretical specific capacity (3860 mA·h·g^{-1}) and lowest reduction potential (-3.040 V vs. standard hydrogen electrode) of the Li metal anode [17]. When a Li anode is paired with a conversion or intercalation cathode with a high specific capacity, the Li battery system can deliver high energy density and is superior to other battery systems. Among such systems, LIBs (which pair Li with an intercalation cathode), Li–S batteries, and Li–O_2 batteries have come under strong consideration, with encouraging progress having been achieved in all three battery systems. Fundamental understanding of these battery chemistries, in terms of the formation process of interphase, the electrode reaction mechanism, and the electrolyte, is deepening and can sustain the further development of rechargeable Li batteries. Moreover, advancements in energy chemical engineering provide strong support for battery research, including proof-of-concept prototype batteries, pilot production, and so on.

The electrolyte is an indispensable component of the battery chemistry for next-generation Li batteries [18]. Currently used electrolytes are divided into two classes: liquid and solid electrolytes. Initial research into batteries involved liquid electrolytes due to their high ionic conductivity and easy access. However, certain inherent features of liquid electrolytes limited the further development of such batteries; for example, their volatility and flammability posed a safety threat even with excellent battery management systems. Hence, solid electrolytes were developed in order to address the strong demand for inherent safety. Nevertheless, the low ionic conductivity of solid electrolytes still hinders their practical deployment in commercial batteries. Furthermore, interfacial impendence between the electrode and solid electrolyte is a critical problem. Tremendous progress has recently been achieved in liquid and solid electrolytes due to the emergence of new materials and technology, promoting research on next-generation Li batteries.

This review summarizes challenges and recent progress related to next-generation Li batteries, with a focus on Li-ion, Li–S, and Li–O_2 batteries with Li metal anodes. Other battery chemistries (e.g., aqueous Li batteries [19–21], silicon anodes [22,23], sodium batteries [24–26], and redox flow batteries [27]) have recently been summarized in other excellent reviews. First, the types and features of liquid and solid electrolytes are summarized and compared to provide a reference for assessing which electrolyte may best be considered for next-generation Li batteries. Current strategies for overcoming the drawbacks of liquid and solid electrolytes are also reviewed. Second, challenges and recent progress in the three most promising Li batteries—Li-ion, Li–S, and Li–O_2 batteries—are examined in retrospect from the perspective of energy chemical engineering science. Finally, an outlook of next-generation Li batteries is presented.

2. Choice of electrolyte

The electrolyte is an indispensable component in a battery system, as it contributes to the formation of ion-conductive pathways and combines with external electron pathways to construct a closed loop. The bulk ionic conductivity of the electrolyte and the connectivity of the ion-conductive channels and electron pathways within the electrodes [28] significantly influence the major internal resistance of a battery. Therefore, increasing the bulk ionic conductivity of the electrolyte and improving the contact area and pattern between the electrolyte and the electrodes are vital for both liquid and solid electrolytes. Furthermore, the stability of electrolytes toward the electrodes is also a prerequisite for its practical application in a working battery [29].

In next-generation rechargeable Li batteries, the aforementioned three prerequisites should be simultaneously satisfied. However, the use of the latest conversion electrodes introduces new challenges. Although liquid and solid electrolytes have unique characters, neither can fully satisfy all the requirements. Which type of electrolyte is most compatible for next-generation Li batteries? The following sections briefly discuss this question.
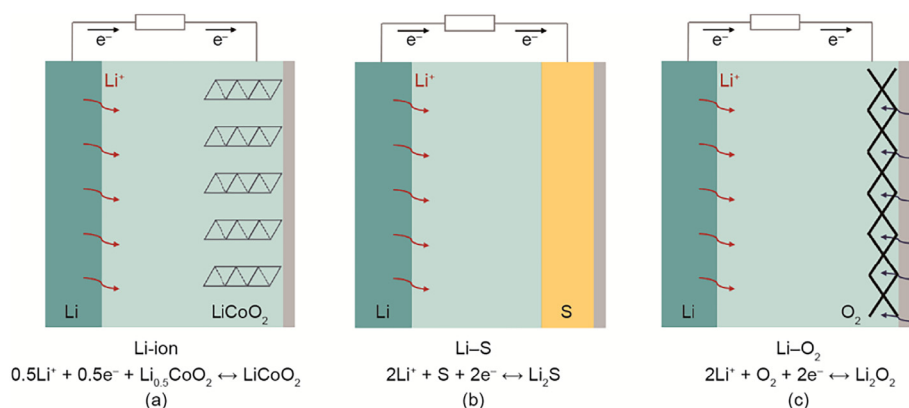

Li-ion
$0.5Li^+ + 0.5e^- + Li_{0.5}CoO_2 \leftrightarrow LiCoO_2$
(a)

Li–S
$2Li^+ + S + 2e^- \leftrightarrow Li_2S$
(b)

Li–O_2
$2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$
(c)

Fig. 1. Schematics of Li-ion, Li–S, and Li–O_2 batteries based on non-aqueous liquid electrolytes.

2.1. Liquid electrolytes

A liquid electrolyte mainly consists of a non-aqueous solvent, Li salts, and other additives [30]. The advantages of a liquid electrolyte include its high ionic conductivity of about 10 mS·cm^{-1} at room temperature and its excellent contact with porous electrodes, which permit the construction of highly effective and interconnected ion pathways [31–34]. Therefore, liquid electrolytes are employed in most batteries today, including commercial batteries and the lab-scale investigation of next-generation Li batteries [35]. The development of liquid electrolytes has already been traced in impactful and insightful reviews [18,30,34,36,37].

The success of liquid electrolytes in LIBs can be attributed to the stable solid electrolyte interphase (SEI) that forms on most anodes and cathodes, which prevents constant side reactions and ensures the stable cycling of batteries [30,38]. However, when it comes to conversion electrodes in next-generation Li batteries, a stable SEI no longer maintains easily owing due to the drastic changes in volume and crystal during charge and discharge, which limit the lifespan of Li batteries and sometimes threaten the safety of batteries [39]. The growth of Li dendrites induced by an uneven and unstable SEI can penetrate the separator, leading to short circuit and thermal runaway. In addition, the intermediate discharge products of conversion electrodes, such as polysulfides in Li–S batteries, can dissolve and diffuse in the liquid electrolyte, which further endangers the originally brittle SEI on the Li anode and can easily cause the battery to overcharge [40]. The intermediate discharge products in Li–O$_2$ batteries, such as the oxygen radical O$^{·2-}$, can rapidly react with liquid electrolytes and destroy the stability of the whole battery system [41].

Therefore, a specific electrolyte formulation should be chosen for a specific battery chemistry, after many trial-and-error experiments and with the guidance of simulations. The electrochemical stability window, chemical stability toward electrodes, wetting ability, cost, and other factors should be considered when choosing a liquid electrolyte.

There are two main types of commonly used liquid electrolytes: carbonate electrolytes for Li-ion batteries, and ether electrolytes for Li–S and Li–O$_2$ batteries. For Li-ion batteries, 4 V- or 5 V-class cathode is employed; therefore, the electrolyte should be able to tolerate a high voltage. Hence, a carbonate electrolyte is chosen instead of an ether electrolyte. The electrochemical stability window of carbonate electrolytes is greater than 4.3 V, which is higher than that of an ether electrolyte (< 3.5 V) in dilute electrolyte. For Li–S and Li–O$_2$ batteries, the voltage is usually less than 3.5 V. Moreover, polysulfides and oxygen radicals can react with carbonate solvents, causing irreversible damage to the electrolyte. Therefore, ether electrolytes with high chemical stability are commonly employed. To summarize, the unique features of different liquid electrolytes should be taken into consideration when choosing an electrolyte.

In addition, the inherent disadvantages of liquid electrolytes, such as their limited electrochemical stability window, volatility, flammability, and leakage, are hindrances to their use as promising candidates for next-generation Li batteries, which require increased safety and environmental friendliness.

To overcome these drawbacks of liquid electrolytes and render them appropriate for next-generation Li batteries, great progress has been made in electrolyte formulation in terms of solvent, Li salts, and additives, with a focus on stabilizing the SEI, suppressing the dissolution and reaction of intermediate discharge products, widening the electrochemical stability window, and improving the nonflammability of liquid electrolytes when coupled with conversion electrodes. New electrolyte formulations are continually emerging, such as concentrated electrolytes [42–44] and fluorinated electrolytes [45,46]. In spite of significant advances, the practical demands for a liquid electrolyte are far from being met. However, new efforts are ongoing.

2.2. Solid electrolytes

Solid electrolytes have drawn a great deal of attention as substitutes for liquid electrolytes [10,47–49]. In addition to overcoming the inherent drawbacks of liquid electrolytes such as volatility, flammability, and leakage, the mechanical strength of solid electrolytes is much higher than that of liquid electrolytes, and can suppress penetration by Li dendrites. The polysulfides in Li–S batteries cannot dissolve in a solid electrolyte, so the severe shuttle effect that exists in liquid electrolytes can be avoided. However, the discharge and charge mechanisms of a sulfur cathode change when a solid electrolyte is used. The stability of the solid electrolyte toward the oxygen radical, O$^{·2-}$, is enhanced in Li–O$_2$ batteries due to the reduced reactivity. Furthermore, the calculated electrochemical stability window of a solid electrolyte is generally greater than 5 V, which is higher than that of a liquid electrolyte [50,51]. When a solid electrolyte is applied in a practical battery system, its electrochemical stability window may decrease significantly. For example, the decomposition of sulfide solid electrolytes is facilitated in full batteries due to carbon in the electrodes [52].

In general, solid electrolytes can be classified into two types: polymer and inorganic electrolytes [53]. The ionic conductivity of a solid electrolyte is usually lower than that of a liquid electrolyte at room temperature, as solid and liquid electrolytes have totally different lithium ion-transportation mechanisms. The ionic conductivity of a polymer electrolyte is around 10^{-6}–10^{-5} S·cm^{-1} at room temperature, whereas the ionic conductivity of an inorganic solid electrolyte is around 10^{-5}–10^{-3} S·cm^{-1} [10]. In addition to its inherent ionic conductivity, the thickness of a solid electrolyte is important. If a solid electrolyte is too thick, the internal resistance of the working battery will be considerably higher than that of a battery with a liquid electrolyte [54].

In the last three decades or more, the ionic conductivity of solid electrolytes has increased significantly, such that it is foreseeable that ionic conductivity may no longer be the greatest obstacle in the future development of practical solid electrolytes. Rather, the main obstacle now comes from the interfaces between solid electrolytes and the electrodes [55,56]. The electrode in a practical battery is usually solid and porous. Thus, the interfaces between a solid electrolyte and the electrodes are connected in a "dot-to-dot" style, compared with the wetting of the electrode materials that occurs with liquid electrolytes. As a result, the interfacial resistance of a battery with a solid electrolyte is much greater due to poor contact, which deteriorates the performance of the battery. The interfacial resistance between a polymer electrolyte and the electrodes is less than that between an inorganic solid electrolyte and the electrodes, due to a larger effective contact area. However, it is necessary to reduce the interfacial resistance further in order for such batteries to be practical in operation. In recent years, several methods have been promoted to decrease interfacial resistance. These include *in situ*-formed SEI [57,58] and an inorganic coating on the electrolyte [59–63]. The effectiveness of these methods over a long cycle life with dynamic interfaces should be investigated further.

The unique features of each type of solid electrolyte must be considered when choosing an electrolyte for a specific type of battery chemistry within a working battery. The application of a polymer electrolyte is generally limited to 4 V-class batteries, which employ LFP as the cathode, due to the inherently limited electrochemical stability window of polymer electrolytes.

Inorganic electrolytes can be classified into several types, such as oxide, sulfide, and hydride electrolytes, among others. Oxide-based solid electrolytes have high chemical and electrochemical

stability, high mechanical strength, and a high electrochemical oxidation voltage, making it feasible to use these electrolytes in batteries with a high-voltage cathode (> 4 V). However, oxide-based solid electrolytes are brittle and expensive in large-scale production. Sulfide-based solid electrolytes have the advantages of high conductivity, good mechanical strength, good mechanical flexibility, and low grain-boundary resistance. However, their application is limited by their low oxidation stability, sensitivity to moisture, and poor compatibility with cathode materials. Thus, the rational choice of a solid electrolyte should be based on a comprehensive understanding of each type, and on the understanding that each solid electrolyte has its own limitations.

Solid electrolytes have certain inherent drawbacks: Both the cost and the complexity of the fabrication of solid electrolytes significantly restrict their scalable production. Furthermore, side reactions occur on the surface of a solid electrolyte when exposed to water or humid air [64,65], changing the original features of the solid electrolyte. Therefore, strict preservation conditions are required. When in contact with a Li anode, side reactions also occur for most solid electrolytes; the resulting decomposition products further complicate the interfacial issues [66,67]. It is still unclear whether detrimental reactions occur for cathode sides, so more investigation is required.

To summarize, solid electrolytes are attractive in their ability to overcome several significant problems facing next-generation Li batteries, such as Li dendrites and the polysulfide shuttle effect. However, both challenges and opportunities exist in the exploration of solid electrolytes for rechargeable batteries, including ion transportation in multiphase, interfacial structure and components, the dynamic evolution of interfaces in a working battery, surface stability, cost and materials processing, and compatibility with cell assembly manufacturing.

3. Lithium batteries

Li batteries are endowed with high energy density due to the extremely high theoretical specific capacity (3860 mA·h·g^{-1}) and lowest reduction potential (−3.040 V vs. standard hydrogen electrode) of the Li anode. Therefore, Li batteries have attracted a great deal of interest and investment as promising candidates for next-generation batteries.

The study of Li batteries began in the 1950s. Commercial Li batteries were released onto the market by Moli Energy Corporation, but failed because the batteries frequently caught on fire. When Li batteries catch on fire, it is usually a result of dendrite growth—a problem that still hinders the practical application of Li batteries today. Due to advances in nanotechnology, computational simulation, and advanced characterization technologies, the fundamental understanding of the formation and growth of Li dendrites has increased, and several strategies to protect the Li anode have emerged in recent years. Li anode can be paired with an intercalation or conversion cathode in order to construct a full battery. As mentioned earlier, Li-ion, Li–S, and Li–O$_2$ batteries are the three most representative candidates of Li batteries. A conservative estimate places the energy density of these batteries at greater than 300 W·h·kg^{-1}, and perhaps as high as 500 W·h·kg^{-1} under practical conditions in future. Moreover, several advanced liquid and solid electrolytes have been demonstrated to be compatible within these batteries in the laboratory, thus providing more possibilities for next-generation Li batteries.

As mentioned above, drastic volume change, poor reversibility of electrode reactions, and complex interfacial issues are inevitable while using conversion electrodes. In addition, specific issues must be addressed for Li-ion, Li–S, and Li–O$_2$ batteries, respectively, due to the different conversion cathodes. Specific issues

and corresponding solutions have been thoroughly reviewed in recent insightful publications for Li-ion [6,7,39,68], Li–S [40,69,70], and Li–O$_2$ [41,71,72] batteries. The current review will briefly summarize the key scientific and technological issues, historical research, and latest progress in Li-ion, Li–S, and Li–O$_2$ batteries, with the goal of providing future scenarios for next-generation Li batteries.

3.1. Li-ion batteries

The LIBs discussed in this review differ from the commercial LIBs that are presently on the market, as the former employ a Li metal anode to replace the typical graphite anode (Fig. 1(a)). The matched cathodes can be comprised of layered LCO, spinel LMO, layered NMC with different stoichiometries, layered NCA, or olivine LFP. Conversion reactions occur on the anode, and intercalation reactions occur on the cathode. Compared with commercial LIBs, the use of a Li anode increases the energy density by decreasing the mass of the anode and improving the quantity of cathode. The lower reductive potential of the Li anode (0.2 V lower than that of a graphite anode) also contributes to the increase in energy density. Compared with Li–S and Li–O$_2$ batteries, LIBs have fewer technical challenges because intercalation cathodes are relatively more stable than conversion cathodes. LIBs with a Li metal anode may be the first to have a major breakthrough toward practical application. However, challenges and opportunities coexist. At present, the challenges that must be dealt with in the development of LIBs mainly come from the Li anode, the electrolyte, and the interface.

Li anode can react with almost any electrolyte due to its extremely low reduction potential. Its reaction products constitute the SEI on the Li anode, which was first named by Peled in 1979 [73]. The generated SEI is heterogeneous and fragile, and has varied spatial resistance; it initially induces uneven Li deposition underneath and eventually induces Li dendrites by means of a self-amplifying process [32]. During the repeated charge and discharge processes, Li dendrites give rise to low coulombic efficiency, constant electrolyte consumption, cracking and repair of the SEI, and the formation of a considerable amount of dead Li [74]. As mentioned earlier, Li dendrites can even penetrate the separator and connect with the cathode, leading to a short circuit and fire (Fig. 2) [6]. Therefore, Li dendrites have a significant negative effect on the stabling cycling of batteries. In Li batteries, the formation and growth of Li dendrites can be suppressed and even avoided by forming a uniform and stable SEI, which is necessary in order for these batteries to achieve practical application.

Considerable effort has been devoted to understanding and suppressing the formation and growth of Li dendrites since the 1950s [7,39]. A fundamental understanding of the formation and growth of Li dendrites is a prerequisite for developing effective strategies to suppress Li dendrites. With the help of advanced characterization tools, such as electron microscopes [75,76], spectral analyzers
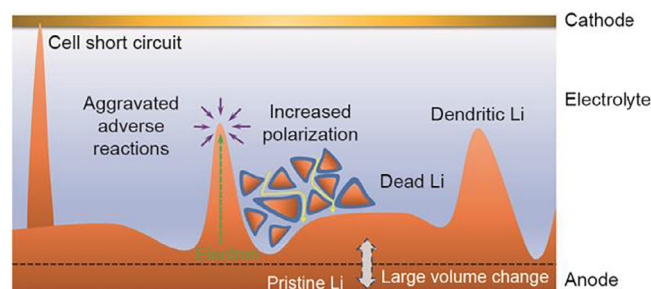

Fig. 2. Challenges affecting the Li anode in rechargeable batteries. (Reproduced from Ref. [6] with permission of American Chemical Society, © 2017)

[77,78], electrochemical analyzers [79–82], and isotope labeling [83,84], the components and structure of the SEI are gradually being disclosed. The SEI is composed of both inorganics (Li_2O, Li_2CO_3, and LiF) and organics (ROLi, $ROCO_2Li$, RCOOLi) (Fig. 3(a)) [73]. The structure of the SEI is currently viewed in terms of the mosaic model and the multilayer model [85]. Recently, Cui and co-workers [76,86] investigated the components and structure of SEI using cryo-electron microscopy to preserve the pristine SEI furthest. The mosaic and multilayer structures of the SEI have also been witnessed in different electrolytes. In an electrolyte containing fluoroethylene carbonate (FEC), an ordered multilayer SEI was observed to favor the uniform Li stripping and reduce the Li loss during cycling. The crystalline grain distributions within the SEI are the critical difference between a mosaic SEI and a multilayer SEI (Fig. 3(b)) [86]. They observed that Li dendrites preferred to grow along the <111> in carbonate electrolytes, in terms of single-crystalline nanowires. In addition to experimental tools, computational simulations contribute to an understanding of the deposition behavior of Li and the decomposition of the electrolyte [87]. Brissot, Chazalviel, and co-workers [88,89] correlated the formation of Li dendrites with concentration gradients by simulations. When the ionic concentration drops to zero with a large current density on the negative electrode, at a time known as Sand's time, Li dendrites are initiated. All of the models that have been reported were obtained based on specific conditions, so each has its own limitations when being applied to a practical system.

Many strategies have been proposed to suppress Li dendrite, in line with the increasing fundamental understanding of the formation and growth of dendrites. *In situ* SEI formation, an *ex situ* coating or barrier layer, and structured Li anodes are the main strategies for suppressing the formation of Li dendrites [7,90].

In situ SEI formation focuses on improving the uniformity and stability of the SEI by regulating the electrolyte components—that is, the solvents [45,91], Li salts [92–94], and additives [95–100]. Li ions are solvated by solvents, anions, and additives, forming a solvation sheath with specific components and a specific structure [101]. The solvation sheath of the Li ions significantly affects the components and structure of the SEI that forms. The solvents and anions in the solvation sheath preferably react with the Li anode, compared with free solvents and anions, and their decomposition products dominate in the SEI. The solvents in the solvation sheath are also selective. Cyclic carbonate solvents are preferably recruited into the solvation sheath, in comparison with linear carbonate solvents, which affects the subsequently formed SEI (Fig. 4(a)) [102]. Even when they are within the solvation sheath at the same time, solvents such as FEC and ethylene carbonate (EC) have a preferred order [103]. In addition, Li salts and additives in the solvation sheath significantly impact the uniformity and stability of the SEI. Recently, Zhang and co-workers [104,105] recently demonstrated that uniform Li deposition and stable cycling can be achieved by concurrently regulating the solvents and anions in the solvation sheath. The introduction of FEC and $LiNO_3$ into the solvation sheath contributes to increasing the content of LiF and LiN_xO_y in order to promote Li diffusion and uniform deposition (Fig. 4(b)) [104]. Furthermore, the concentration of Li ions also changes the solvation sheath [42,46,93,106]. With an increase in Li concentration, free solvents and anions are gradually solvated. In concentrated electrolytes, the decomposition products of anions dominate in the SEI and determine the uniformity and stability. It has been reported [93] that 4 mol·L^{-1} Li bis(fluorosulfonyl)imide (LiFSI) in dimethoxyethane (DME), as proposed by Zhang and co-workers, has been proved to be effective in improving coulombic efficiency and regulating uniform Li deposition (Fig. 4(c)) [93,94].

As an alternative, *ex situ* coating or a barrier layer has been proposed in order to block dendrites. High mechanical strength, uniformity of Li ion flux, and low interfacial resistance are three prerequisite conditions for *ex situ* coating to be employed in Li batteries [7]. Thus far, carbon materials [107–109], polymers [110–113], and inorganics [114–118] are the preferred choices for *ex situ* coating. Carbon materials have been chosen for *ex situ* coating due to their high mechanical strength, high electrical conductivity, excellent chemical and electrochemical stability, and tunable structures. Cui and co-workers [119] designed an *ex situ* coating using interconnected hollow carbon nanospheres in order to avoid the penetration of Li dendrites and prevent cracks in the SEI. This carbon coating also regulated Li ion plating to form columnar Li deposition (Fig. 5(a)) [119]. Polymers have been chosen for *ex situ* coating due to their flexibility, controllability, and diversity. A polymer with high chemical/electrochemical stability is essential in order to adapt to the extremely high reactivity of the Li metal anode. Guo, Wen, and co-workers [120] designed a flexible and smart Li polyacrylic acid (LiPAA) ex-coating to accommodate the dynamic volume change during Li plating/stripping processes by means of self-adapting interface regulations (Fig. 5(b)) [120]. This smart coating could significantly reduce the side reactions and improve battery safety, due to the high elasticity and stability of the LiPAA polymer. Inorganic materials with high mechanical strength, including inorganic solid electrolytes, have also been
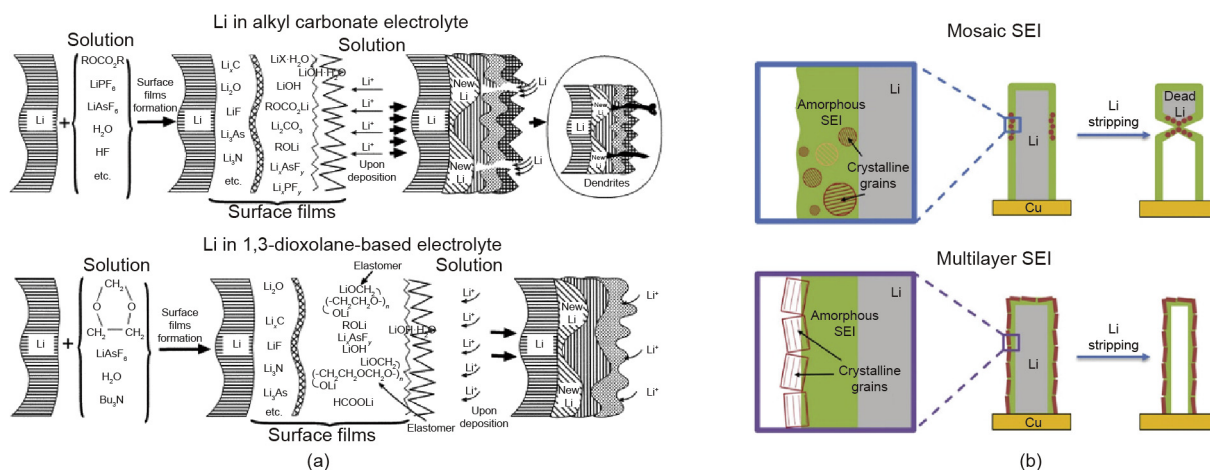
Fig. 3. (a) Scheme of SEI formation on the Li anode in alkyl carbonate and in 1,3-dioxolane-based electrolytes. (b) Schematic of the mosaic and multilayer SEI nanostructures and the corresponding effects on the Li stripping process. ((a) Reproduced from Ref. [73] with permission of Elsevier, © 2000; (b) reproduced from Ref. [86] with permission of Elsevier, © 2018)
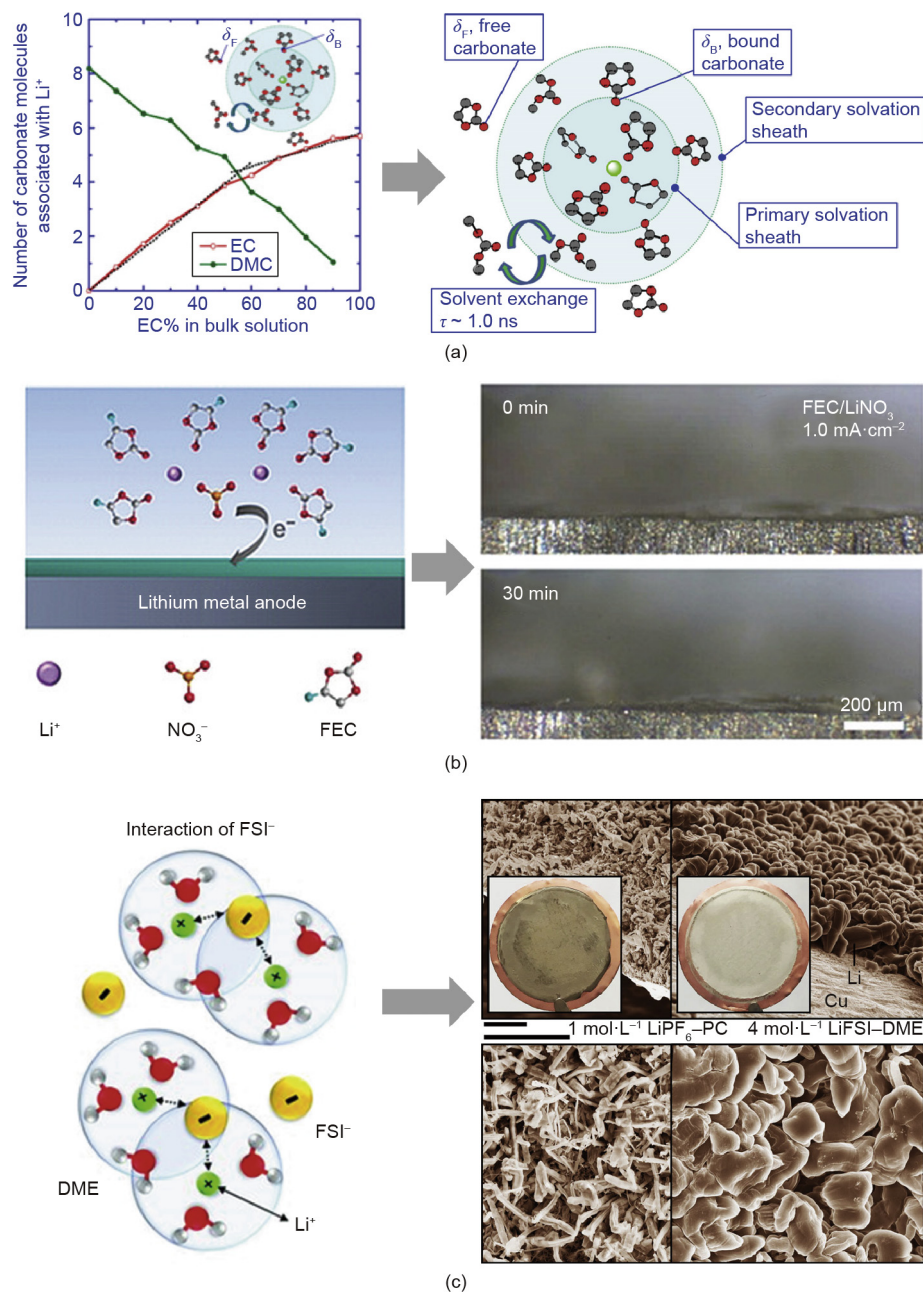
Fig. 4. (a) Schematic of the solvation sheath of Li ions in non-aqueous electrolytes, and the change of the solvation sheath with increased EC content. DMC: dimethyl carbonate. (b) Schematic of the solvation sheath of Li ions while FEC and LiNO₃ are concurrently present, and corresponding *in situ* optical images of the Li deposition process. (c) A solvation sheath of Li ions in concentrated electrolyte, and the corresponding Li deposition morphology (scale bar, 10 μm). PC: propylene carbonate. ((a) Reproduced from Ref. [102] with permission of American Chemical Society, © 2013; (b) reproduced from Ref. [104] with permission of Wiley, © 2018; (c) reproduced from Ref. [94] with permission of American Association for the Advancement of Science, © 2015, and from Ref. [93] with permission of the authors under the terms of the CC-BY 4.0 license, © 2015)

chosen as promising *ex situ* coating materials. However, inorganics are generally brittle and require complex materials processing. Therefore, a rational combination of inorganic materials and polymers is a possible choice for constructing an *ex situ* coating that is both flexible and rigid [121]. An artificial soft–rigid protective layer, in which poly(vinylidene-*co*-hexafluoropropylene) (PVDF-HFP) acts as the soft part and LiF acts as the rigid part, was recently proposed by Huang and co-workers (Fig. 5(c)) [122]. The layer was able to suppress Li dendrites and prevent the random floating of isolated Li in order to form a stable interface, which guarantees long stable cycling for a battery. Composite solid electrolytes have been used to suppress Li dendrites in Li batteries [123]. Anions were tethered

to provide a higher Li transference number [124], and uniform Li ion flux and deposition were achieved. Composite solid electrolytes also exhibited good stable cycling in all solid-state batteries.

Constructing a structured Li anode is another way to suppress Li dendrite formation [125–129]. The biggest advantage of structured Li anode is that it can reduce the real current density due to its large surface area, much pore and connecting structures [130]. As indicated by the aforementioned Sand's time model, a lower current density leads to a greater Sand's time. Thus, the formation of Li dendrites is delayed by a low real current density. To further guide Li ions to deposit uniformly on a structured anode, lithiophilic sites have been proposed. For example, ZnO [131,132], Si
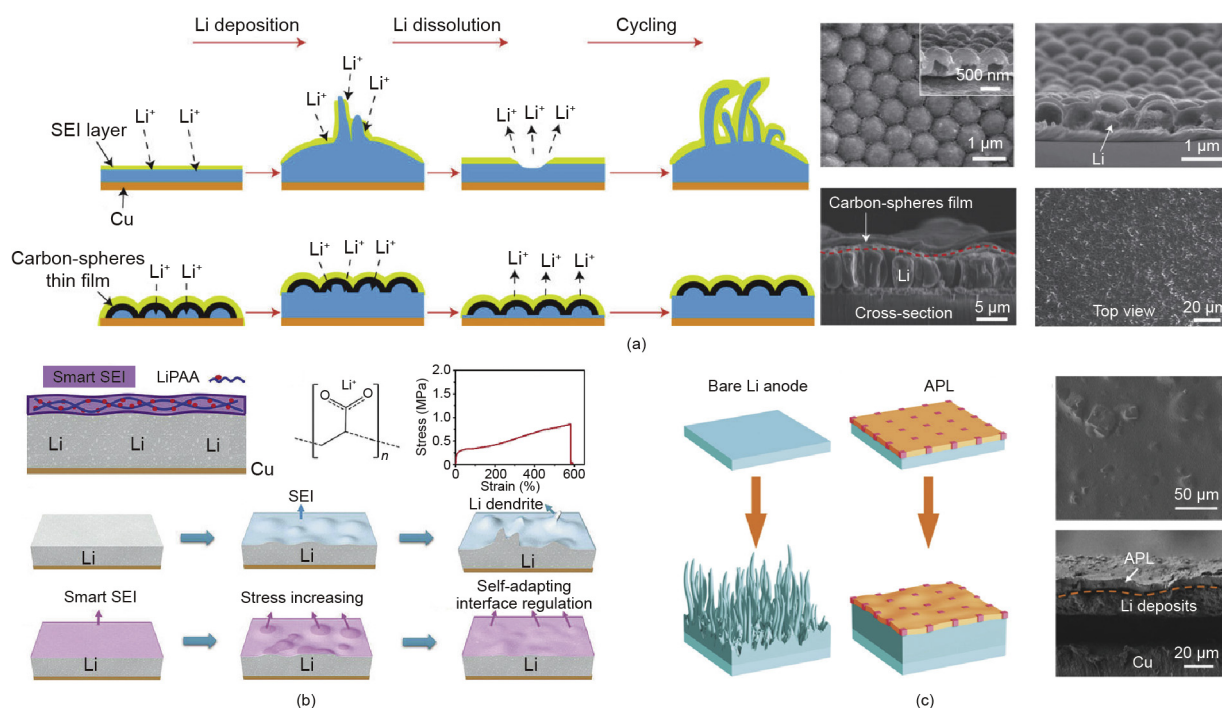
Fig. 5. (a) The carbon nanosphere coating serves as an artificial layer to protect the Li anode (blue). (b) A flexible coating suppresses Li dendrites by means of self-adapting interface regulation. Inset: Chemical structure and stress–strain curve of the LiPAA gel polymer. (c) A soft–rigid artificial layer designed to protect the Li anode from the growth of dendrites. APL: artificial protective layer. ((a) Reproduced from Ref. [119] with permission of Nature Publishing Group, © 2014; (b) reproduced from Ref. [120] with permission of Wiley, © 2017; (c) reproduced from Ref. [122] with permission of Wiley, © 2018)

[133], nitrogen (N)-doped graphene [134], and MgO [135] have been confirmed to be lithiophilic. N-doped graphene was adopted as a structured Li anode in order to regulate Li nucleation and suppress dendrite formation (Fig. 6) [134]. The pyridinic and pyrrolic nitrogen in the N-doped graphene is lithiophilic, and thus guides Li nucleation to achieve uniform Li deposition.

The discussion above reviewed the challenges of employing Li metal as an anode and summarized the strategies that may be used to overcome these issues. In addition to the issues related to Li anodes, the high specific capacity of the cathode presents challenges. Ni-rich and Li-rich cathode materials have been developed. However, the inherent stability of these materials is poor, due to
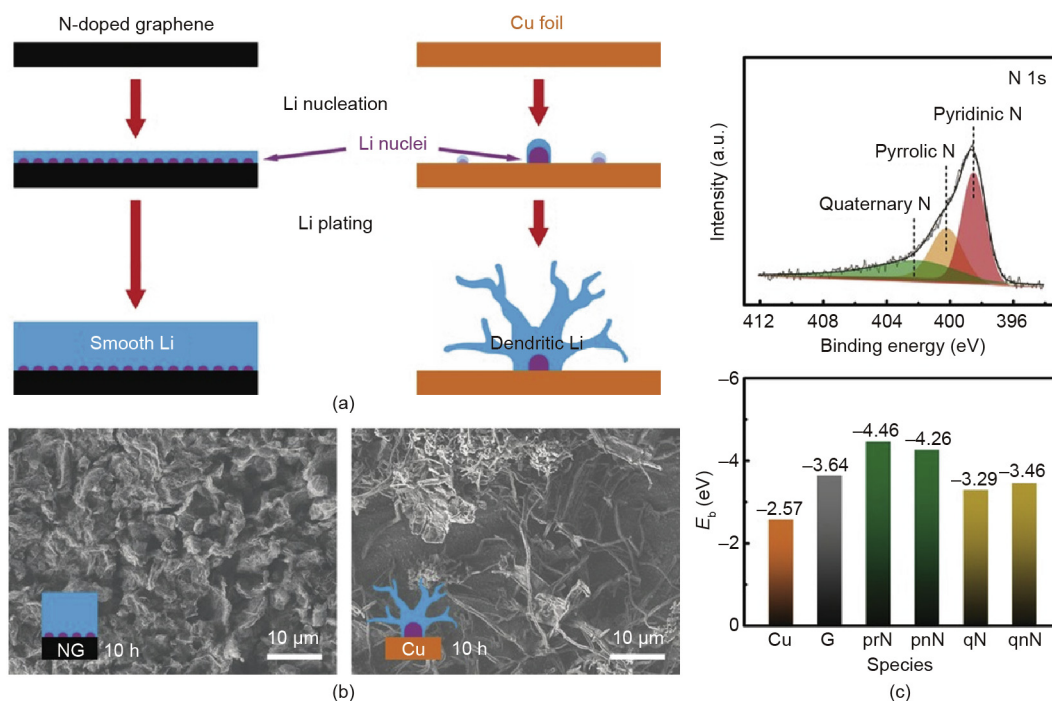
Fig. 6. (a) Schematic of the Li nucleation and growth process on N-doped graphene (NG) and Cu foil; (b) the morphology of Li deposition on NG and Cu foil electrode; (c) N species and their binding energy (E_b) with Li. G: graphene; prN: pyrrolic nitrogen; pnN: pyridinic nitrogen; qN: quaternary nitrogen on the edge; qnN: quaternary nitrogen in the bulk phase. (Reproduced from Ref. [134] with permission of Wiley, © 2017)

the irreversible changes that occur in the crystal structure and the interfacial phase, such as Li/Ni mixing, the formation of micro-cracks, and the highly reactive surface [136,137]. The dissolution of transition metal ions also destroys the SEI on the anode. To utilize a more specific capacity, the batteries must be charged above 4.5 V or even 5.0 V, which is challenging for the stability of cathode [138,139]. The electrolyte must also be updated in order to tolerate the concurrent high reductive and oxidative reactivity.

In summary, the major challenges affecting the development of LIBs originate from the Li anode. Many effective strategies have been applied in the laboratory to overcome the formation and growth of Li dendrites. Recent advances in improving the utilization of the Li anode are summarized in Table 1 [45,91,93,104,112,140–143]; the examples provided here are more attractive in regard to practical application than those in other publications. The combination of electrolyte formulation and a structured anode is a promising direction. For practical applications, LIBs should be tested under lean electrolyte conditions, such as in pouch cells. LIBs still have a long way to go before they can become the next-generation Li batteries.

3.2. Li–S batteries

Li–S batteries, which are comprised of a Li anode and a S cathode (Fig. 1(b)), are capable of utilizing a multi-electron electrochemical reaction between S and Li to release higher energy density. The discharge process shows two plateaus at 2.3 and 2.1 V in ether liquid electrolytes; the upper and lower plateaus have been assigned to the conversion of S_8 to Li_2S_4 and that of Li_2S_4 to Li_2S, respectively (Fig. 7(a)) [40,70]. The final discharge product is Li_2S. In the subsequent charge process, Li_2S is converted to S_8 and undergoes the formation of a lithium polysulfide intermediate. S and Li are lightweight elements, which gives them a high specific capacity of 1672 and 3860 mA·h·g^{-1}, respectively. Therefore, the theoretical energy density of Li–S batteries is as high as 2600 W·h·kg^{-1} [15,69]. Even considering the other parts of a battery at the pack level, the energy density may still be greater than 400 W·h·kg^{-1}. In addition, sulfur is abundant and low in cost, which decreases the entire cost of Li–S batteries and makes them competitive as a form of clean energy storage system in the future [144,145]. Unlike Li–O$_2$ batteries, Li–S batteries operate in a closed system, which prevents potential explosive danger when the components are exposed to air. The high energy density, low cost, and relative safety of Li–S batteries make them attractive candidates for next-generation Li batteries.

However, many issues still plague the development of Li–S batteries (Fig. 7(b)) [69]. In general, the cathodic materials in Li–S batteries comprise elemental sulfur in order to adequately utilize the advantages of the multi-electron conversion reaction. Lithiated sulfur, either polysulfides or Li_2S_2/Li_2S, can be also used

Table 1
Recent advances in improving the coulombic efficiency (CE) of Li|Cu batteries based on liquid electrolyte.

Label	Category	Strategy	Coulombic efficiency	Electrolyte	Year & Ref.
1	Electrolyte	High-concentration electrolyte	98.4% (4.0 mA·cm^{-2}, 1.0 mA·h·cm^{-2}, 1000 cycles)	4.0 mol·L^{-1} LiFSI in DME	2015 [93]
2	Electrolyte	Dual-salts electrolyte with 0.05 mol·L^{-1} LiPF$_6$	—	0.6 mol·L^{-1} LiTFSI + 0.4 mol·L^{-1} LiBOB + 0.05 mol·L^{-1} LiPF$_6$ in EC/EMC	2017 [140]
3	Electrolyte	FEC co-solvent	98.5% (0.5 mA·cm^{-2}, 1.0 mA·h·cm^{-2}, 40 cycles)	1.0 mol·L^{-1} LiPF$_6$ in FEC/DMC	2017 [91]
4	Electrolyte	FEC co-solvent with LiNO$_3$	—	1.0 mol·L^{-1} LiPF$_6$ + 0.2 mol·L^{-1} LiNO$_3$ in FEC/DMC/DME	2018 [104]
5	Electrolyte	Fluorinated solvent	99.2% (0.5 mA·cm^{-2}, 1.0 mA·h·cm^{-2}, 500 cycles)	1.0 mol·L^{-1} LiPF$_6$ FEC/FEMC/HFE	2018 [45]
6	Structured anode	N-doped graphitic carbon foams	99.6% (2.0 mA·cm^{-2}, 4.0 mA·h·cm^{-2}, 300 cycles)	1.0 mol·L^{-1} LiTFSI in DOL/DME with 2% LiNO$_3$	2018 [141]
7	Artificial coating	PDMS film with nanopores	98.2% (1.0 mA·cm^{-2}, 1.0 mA·h·cm^{-2}, 100 cycles)	1.0 mol·L^{-1} LiTFSI in DOL/DME	2017 [112]
8	Artificial coating	Cu$_3$N + SBR composite artificial SEI	97.4% (1.0 mA·cm^{-2}, 1.0 mA·h·cm^{-2}, 100 cycles)	1.0 mol·L^{-1} LiPF$_6$ in EC/DEC with 10% FEC	2017 [142]
9	Artificial coating	3D glass fiber cloth	98.0% (0.5 mA·cm^{-2}, 0.5 mA·h·cm^{-2}, 90 cycles)	1.0 mol·L^{-1} LiTFSI in DOL/DME with 2% LiNO$_3$	2016 [143]

LiTFSI: Li bis(trifluoromethane sulfonyl)imide; LiBOB: Li bis(oxalato)borate; EMC: ethyl methyl carbonate; FEMC: fluoroethyl methyl carbonate; HFE: 1,1,2,2-tetrafluoroethyl-2′,2′,2′-trifluoroethyl ether; DOL: 1,3-dioxolane; PDMS: poly(dimethylsiloxane); SBR: styrene butadiene rubber; DEC: diethyl carbonate.
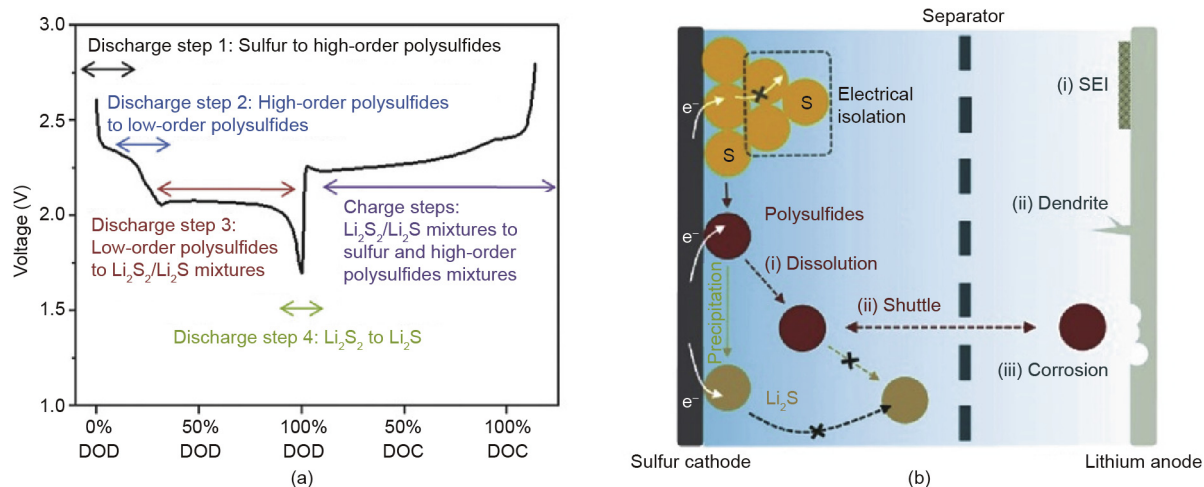
Fig. 7. (a) Illustration of the two plateaus and the corresponding electrochemical reaction steps in Li–S batteries. DOD: depth of discharge; DOC: depth of charge. (b) Schematic of the issues affecting Li–S batteries. ((a) Reproduced from Ref. [70] with permission of Wiley, © 2018; (b) reproduced from Ref. [69] with permission of Wiley, © 2017)

as starting electrode materials. In fact, the electrochemical characteristics of lithiated sulfur are the same as those of elemental sulfur after the first cycle [69]. One of the major obstacles in the utilization of elemental sulfur as a cathode is the inherently low electronic conductivity of its discharge product, Li_2S ($\sim10^{-30}$ S·cm^{-1} at 25 °C). The evident structural and morphological changes that occur during cycling result in poor contact between sulfur and its intermediate discharge products, and the current collector. The intermediate polysulfides dissolve in the ether electrolyte. These dissolved polysulfides can shuttle between the anode and cathode during cycling, and react with the Li anode and S cathode to form an internal chemical reaction loop. These problems give rise to a loss of active material, poor lifespan, and low coulombic efficiency.

Pioneer Li–S batteries were first demonstrated in the 1960s. However, Li–S batteries were hindered by their low specific capacity and rapid capacity, and interest in them faded in subsequent decades. In 2009, Nazar and co-workers [146] proposed the use of a highly ordered and mesoporous carbon, CMK-3, to encapsulate sulfur (Fig. 8(a)). The use of porous and electric carbon materials led to a major breakthrough in the development of Li–S batteries, as it became possible to precisely constrain the sulfur within its conductive channels. This strategy gives Li–S batteries a high specific capacity and stable cycling, and opens up the possibility for further investigation into Li–S batteries.

Present strategies to improve the utilization of sulfur and suppress shuttle include the following: ① employing porous and electric host materials to encapsulate the sulfur, with different kinds of carbon materials commonly being used for this purpose, such as porous carbon, graphene [147,148], carbon nanotubes (CNTs) [147,149,150], hollow carbon [151,152], and their nano-composites [153]; ② introducing a physical or chemical interlayer onto the surface of the S particles, cathode, and separator in order to suppress the diffusion of polysulfides [154,155].

Investigations into porous and electric host materials first focused on non-polar host materials, and then included polar host materials. Non-polar host materials are represented by various kinds of carbon materials. The addition of porous and conductive carbon materials increases the electronic conductivity of a composite cathode in order to improve the utilization of sulfur and achieve a high specific capacity. Therefore, the two main research directions in this area involve designing the porous structure and the electronic conductivity of carbon materials.

Regarding the porous structure of carbon materials, the size, shape, topology, and combination of pores have been optimized for encapsulating sulfur and better suppressing polysulfide dissolution. Archer and co-workers [152] have employed hollow carbon spheres with a diameter of 200 nm to encapsulate sulfur. The hollow structure decreases the loss of active materials by means of physical confinement. Moreover, the side effects induced by the volume change between S and Li_2S are also suppressed by the hollow structure. In general, a Li–S battery shows better performance when hollow-structured host materials are used than when open-structured materials are used.

Regarding improvements in the electronic conductivity of carbon materials, an excellent rate performance and high specific capacity are achieved using CNTs, graphene, and their composites, albeit less than when compared with common porous carbon [156]. Zhang and co-workers [153] have rationally constructed a hybrid nano-architectured graphene/CNT@porous carbon as a sulfur host (Fig. 8(b)). The CNT and graphene contribute to improving
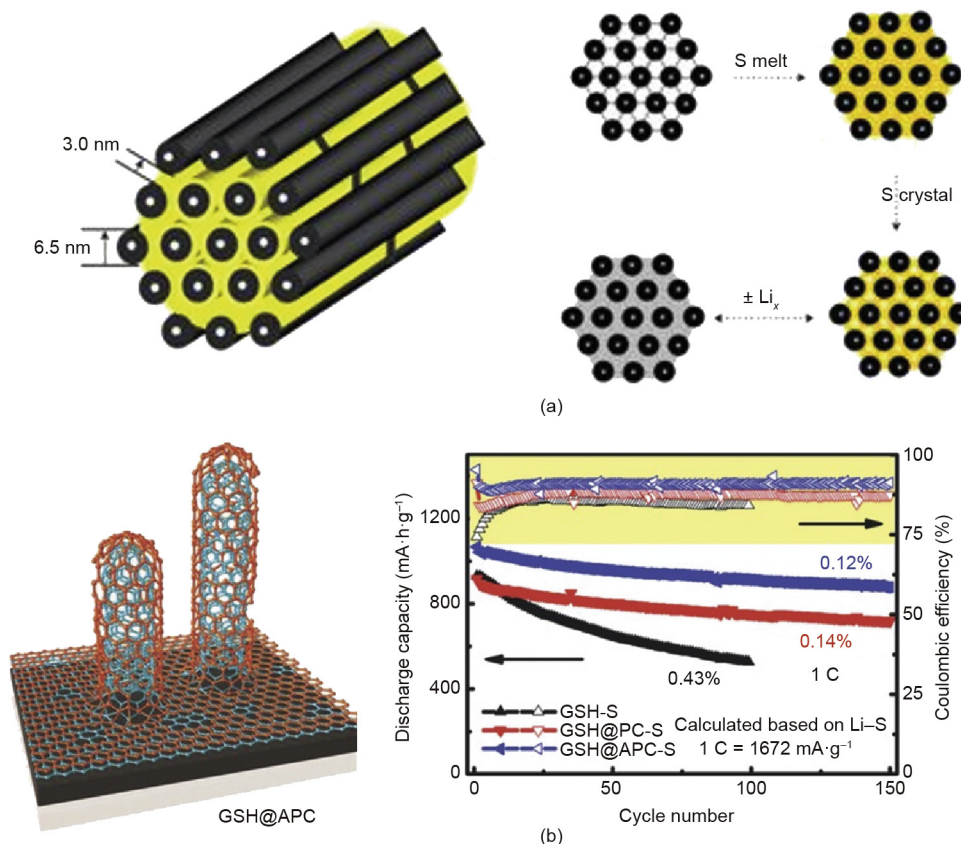

Fig. 8. (a) Schematic of sulfur (yellow) confined in the interconnected pore structure of mesoporous carbon, the synthesis of a composite cathode, and the subsequent discharging–charging with lithium. (b) Schematic of the nano-architectured graphene/carbon nanotube (CNT)@porous carbon hybrid and its performance in Li–S batteries. GSH: graphene/single-wall carbon nanotube (SWCNT) hybrids; PC: pyrolytic carbon; APC: activated pyrolytic carbon. ((a) Reproduced from Ref. [146] with permission of Nature Publishing Group, © 2009; (b) reproduced from Ref. [153] with permission of Wiley, © 2014)

electronic conductivity and bearing the volume change of the active materials, while the porous carbon provides abundant space and acts as a nanoreactor to encapsulate sulfur and confine the polysulfides. The abovementioned carbon materials can also be employed as the interlayer on the separator or cathode in order to intercept and reactivate polysulfides.

Polar host materials have been developed in order to remedy the weak polarity of carbon materials and enhance the combination with polysulfides, thus suppressing their shuttle and increasing sulfur utilization. These materials can be classified into four types: ① N/O/S-doped polymer materials, such as polyaniline [157], polypyrrole [158], and polyethylene glycol [159]; ② N/O/S-doped carbon materials, such as N-doped graphene [160], N-doped hierarchical carbon [161–163], and specific N-containing organic frameworks [164]; ③ inorganic transition metal compounds, such as sulfides [165], oxides [166,167], phosphides [168], and carbides [169]; and ④ organic–inorganic hybrid materials, such as metal–organic frameworks [170]. The stable cycling performance of Li–S batteries is enhanced by the introduction of polar hosts, as compared with non-polar hosts. Zhang and co-workers [171] have demonstrated that both polar and conductive titanium carbide (TiC) can enhance the electrochemical kinetics of a sulfur cathode, facilitating the liquid–liquid transformation

of polysulfides and the liquid–solid nucleation/growth of Li_2S at the same time (Fig. 9(a)). This works confirmed that electronic conductivity is vital for a polar host—information that has further guided the design of host materials for Li–S batteries. Moreover, the proposal of Li bond and the simulations further provided a deep and fundamental comprehension to guide the rational design of cathode materials [172–174].

Nevertheless, host materials are insufficient to totally encapsulate sulfur, and the diffusion of polysulfides toward the anode is inevitable in general cell configurations. To further restrict the diffusion of polysulfides and to reactivate polysulfides, a novel battery configuration has emerged for Li–S batteries. An interlayer on the surface of the cathode or separator and modified separators are introduced with the aim of affecting the electrostatic interaction, chemical effects, and even electronic conductivity. Recent progress in the development of advanced interlayer/separators to improve the stability of Li–S batteries has been achieved in the following aspects: ① shielding the diffusion of polysulfides to the anode and suppressing the shuttle; ② reactivating dead sulfur-containing species in batteries. Polymers [154,175,176], carbons [177–179], oxides [180,181], and their hybrids [148] have been applied as various functional interlayers for better battery performance. Unfortunately, these effects also delay the diffusion of Li
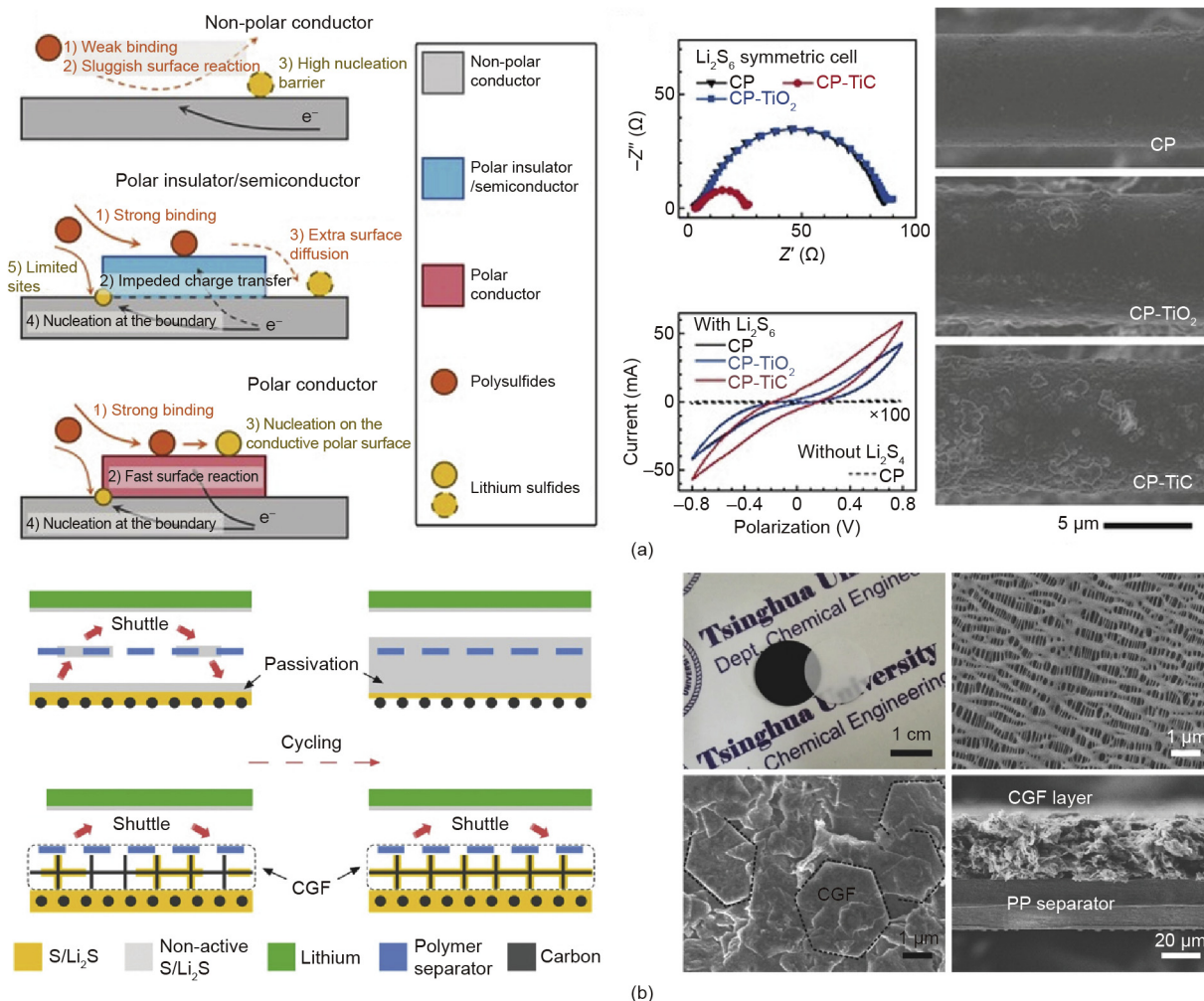
Fig. 9. (a) Illustration of the mechanism of polar host materials in enhancing binding and charge transfer. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) of Li_2S_6 symmetric cells with polar host materials. Scanning electron microscopy (SEM) images of the initial nucleation of Li_2S on different surfaces. CP: carbon-fiber paper. (b) Schematic mechanism of a routine polypropylene (PP) separator and Janus separator with a cellular graphene framework (CGF) layer in suppressing shuttle. SEM images and optical images of the PP separator and Janus separator. ((a) Reproduced from Ref. [171] with permission of Wiley, © 2016; (b) reproduced from Ref. [155] with permission of Wiley, © 2016)

ions and may decrease the rate performance of the batteries. Manthiram and co-workers [177] have reported that a multi-walled CNT interlayer served as a pseudo upper current collector to lower the charge transfer resistance and trap polysulfides. The intrinsic flexibility of the multi-walled CNT interlayer allowed it to endure the volume change during cycling, leading to both a high specific capacity and excellent battery stability. The work demonstrated the enhanced performance of Li–S batteries by designing a new cell configuration with an interlayer, thus opening up a new research field for Li–S batteries. A Janus separator was designed by coating mesoporous cellular graphene framework (CGF)/polypropylene (PP) on the separator in order to promote sulfur utilization (Fig. 9(b)) [155]. The porous PP layer can prevent short circuiting, while the CGF reactivates sulfur-containing species due to close contact with the sulfur cathode.

Most of the strategies described above are achieved with relatively low areal loadings of sulfur (< 2 mg·cm^{-2}). However, this low loading of sulfur is not competitive with commercial LIBs. To pave the way for practical Li–S batteries, a high loading of sulfur is essential, generally higher than 2 mg·cm^{-2}. However, the effectiveness of the abovementioned strategies is doubtful with a high loading of sulfur, which is an essential parameter for practical and viable Li–S batteries.

Moreover, dissolved polysulfides damage the SEI on the Li anode and form a new passivation layer, thus increasing the interfacial resistance [182]. Although LiNO$_3$ is an effective additive for protecting the Li anode [183], this protection decreases with an increased number of cycles. New strategies are required to protect the Li anode and sustain long cycles.

In addition to materials' innovations, the reaction mechanism of the complex multi-electron phase transition is worth investigating, which will provide new opportunities to enhance the performance of Li–S batteries. The recently emerging strategies of redox mediators and reaction promoters [184–186] are representative examples of research that focuses on the fundamental chemical conversion in order to promote practical conditions for Li–S batteries (i.e., high loading of active materials and lean electrolyte). For practical Li–S batteries, the excess mass of lithium and the electrolyte/sulfur (E/S) ratio should be reduced, aside from improving the areal loading of sulfur [187]. Of course, new challenges will emerge; however, these must be solved in order for Li–S batteries to be commercialized in the future.

3.3. Li–O$_2$ batteries

Li–O$_2$ batteries employ oxygen (not natural air at present) as the cathode to pair with a Li anode (Fig. 1(c)). Primary Li–O$_2$ batteries were firstly proposed by Blurton and Sammells [188] in 1979; their rechargeability was then demonstrated in the mid-1990s by Abraham and Jiang [189], who used a carbon substrate for the O$_2$ cathode, a Li anode, and a polyvinylidene difluoride (PVDF) gel electrolyte. In 2006, Bruce and co-workers [190] demonstrated the reversibility of the discharge product, Li$_2$O$_2$, by combining an organic electrolyte with MnO$_2$ as a catalyst. Since then, Li–O$_2$ batteries have gained steep acceleration in terms of R&D effort and are considered to be promising next-generation Li batteries. In general, four types of electrolyte have been employed in Li–O$_2$ batteries: aprotic, aqueous, all-solid-state, and hybrid aqueous/aprotic electrolytes. Among these, aprotic Li–O$_2$ batteries attract the most research effort because aqueous electrolytes have a low decomposition voltage and solid electrolytes have insufficient ionic conductivity [71]. Thus, this section focuses on aprotic Li–O$_2$ batteries. In aprotic Li–O$_2$ batteries, O$_2$ is reduced to solid Li$_2$O$_2$ during the discharge process via the reaction $2Li + O_2 \leftrightarrow Li_2O_2$ (2.96 V vs. Li/Li$^+$) [191]. The charge process is not completely reversible due to the difference between the oxygen reduction reaction (ORR) and the

oxygen evolution reaction (OER). The large overvoltage (~ 0.70 V) between the charge and discharge plateau is direct evidence of this partially reversible reaction. The theoretical energy density of non-aqueous Li–O$_2$ batteries is about 3500 W·h·kg^{-1} when the mass of O$_2$ is included [15]. The O$_2$ cathode is mainly composed of a substrate, catalysts, and binder. O$_2$ is also present as an active material. The substrate provides reaction sites, supports the catalysts, and even catalyzes reversible oxygen electrochemical reactions [192]. Carbon materials, such as black carbon [193], graphene [194], and CNT [195] are the main choices as substrates. As has been proposed by Bruce and co-workers [190], additional catalysts are necessary for fast reaction kinetics. Metal oxides and metal, such as gold (Au) [196], are common catalysts. Since O$_2$ can readily be acquired from the air, the cost of Li–O$_2$ batteries is potentially much lower than that of LIBs. Because Li–O$_2$ batteries operate in an open system, an additional selective membrane is necessary to prevent the permeation of other gases, water, and impurities from the air.

Despite their obvious advantage in energy density, Li–O$_2$ batteries carry both academically and technologically complex problems (Fig. 10) [71]. These challenges mainly originate from the complex chemistry of O$_2$ cathode and high reactivity of Li anode.

- Poor rate capability. The diffusion and dissolution of O$_2$, and the inherent reaction kinetics are bottleneck. The discharge product, Li$_2$O$_2$, is insoluble in liquid electrolyte and easily clogs the substrate, which impedes the reaction process.
- High charge overvoltage. The ORR and OER, corresponding to the discharge and charge processes, respectively, require catalysts with very high bifunctional reactivity.
- Electrolyte and carbon decomposition. The intermediate product, the oxygen radical O$^{\cdot 2-}$, preferably reacts with the organic electrolyte and even with the substrate via nucleophilic attack, resulting in drastic decomposition.
- Li anode reactivity.

Consequently, Li–O$_2$ batteries are still in their infancy, and their development is more challenging than that of Li-ion and Li–S batteries.

To deal with the aforementioned issues, tremendous projects have been proposed in response to the challenges posed by the substrate, catalysts, and electrolytes of Li–O$_2$ batteries. Regarding electrolytes, many studies have shown that electrolyte stability is a key challenge for aprotic Li–O$_2$ batteries [197]. Therefore, searching for electrolytes that can remain stable in the O$_2$-rich electrochemical environment is the current priority. Carbonate electrolytes are severely unstable due to the catalytic activities of the intermediate discharge O-containing species. Ether electrolytes exhibit excellent stability in the presence of the intermediate discharge O-containing species; however, their electrochemical stability remains doubtful over long-term cycling. Dimethyl sulfoxide (DMSO) and tetraethylene glycol dimethyl ether (TEGDME) are common solvents in Li–O$_2$ batteries at present. Aside from solvents, Li salts and additives require more attention, as they also have a significant effect on the stability of the electrolyte. LiPF$_6$, LiNO$_3$, LiClO$_4$, LiCF$_3$SO$_3$, LiN(SO$_2$C$_2$F$_5$)$_2$, and LiN(SO$_2$CF$_3$)$_2$, among others, have been studied for application in Li–O$_2$ batteries [198–200]. The importance of the anion has also been realized, which provides a new route to enhance stability [201]. Additives are generally redox mediators to reduce overvoltage thermodynamically in OER process and anion receptor to increase the solubility of O$_2$. Anion receptor additives include strong Lewis acids or fluorinated compounds, such as tris(pentafluorophenyl) borane (TPFPB) [202], methyl nonafluorobutyl ether (MFE) [203]. Redox mediators, such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) (Fig. 11(a)) [204] and tetrathiafulvalene (TTF) [205], can reduce the overvoltage. Bruce and co-workers [204] have employed DBBQ to promote the solution phase formation of Li$_2$O$_2$ in a low donor number electrolyte; and it was found
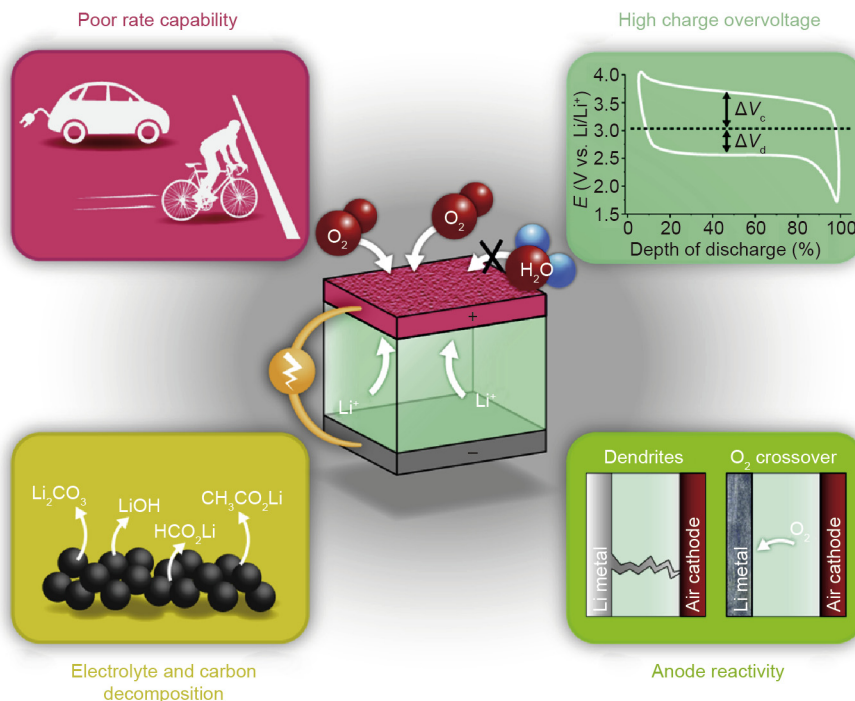
Fig. 10. The challenges of Li–O₂ batteries. (Reproduced from Ref. [71] with permission of Wiley, © 2016)
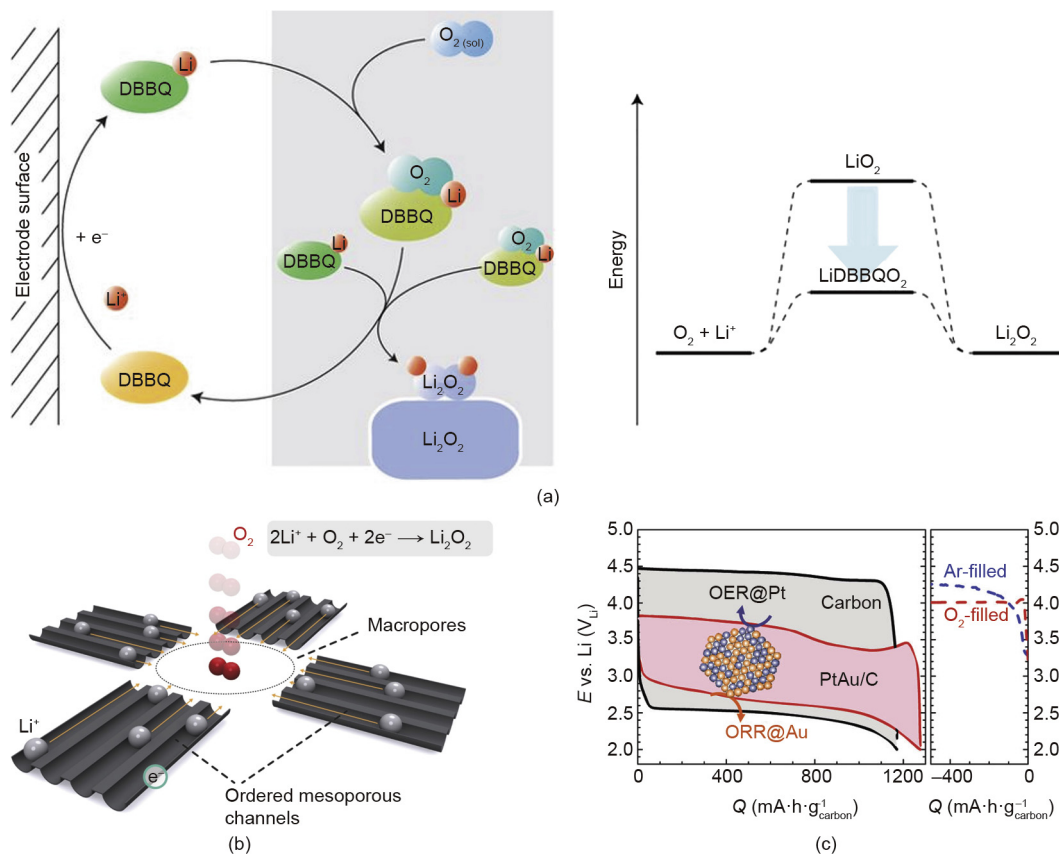

Fig. 11. (a) Schematics of the reaction mechanism of the discharge process and the effect of DBBQ on the potential determining step. (b) Schematic of an ordered hierarchical mesoporous/macroporous carbon catalyst and its effect on O₂/Li₂O₂ conversion. (c) Discharge/charge profiles of carbon and PtAu/C in the third cycle. ((a) Reproduced from Ref. [204] with permission of Nature Publishing Group, © 2016; (b) reproduced from Ref. [213] with permission of Wiley, © 2015; (c) reproduced from Ref. [196] with permission of American Chemical Society, © 2010)

to enhance the discharge performance and exhibit a new mechanism. Other research on the use of ionic liquid and solid electrolyte in Li–O$_2$ batteries is also ongoing [206].

The substrate and catalysts in a Li–O$_2$ battery are designed to decrease the overvoltage, increase energy efficiency, enhance rate performance, and improve self-stability. Carbon materials are the main choice of substrate due to their high conductivity, large surface, high pore volume, and low cost [207,208]. The defects in carbon materials have been found to catalyze the ORR process [209]. Porous carbon materials (e.g., Super P [210], Ketjenblack [211], and Vulcan carbon [212]) have been employed as basic substrates. Their performance can be further enhanced by the design of a new structure, as porous carbon materials with a large pore volume and ordered channels can improve the performance of Li–O$_2$ batteries. Xia, Wang, and co-workers [213] have demonstrated the positive effects of ordered mesoporous channels in facilitating the electron-transfer process and the diffusion of Li ions (Fig. 11(b)). Macropores are surrounded by ordered mesoporous channels in order to provide enough space for the formation/decomposition of Li$_2$O$_2$ and for O$_2$ diffusion.

Catalysts can enhance the reaction kinetics of the OER and/or ORR process, although it remains doubtful whether they can improve the overall performance of a battery. Metal oxides and metals are commonly used catalysts in Li–O$_2$ batteries. MnO$_2$ shows good ORR activity, so Bruce and co-workers [214] have carefully investigated the effect of the crystal structure and morphology of MnO$_2$ in enhancing battery performance. Iridium oxide and ruthenium oxide have also attracted great interest for their excellent OER activity. Metals such as platinum, palladium, gold, and hybrids have also been employed. As the main example of such usage, Shao-Horn and co-workers [196] have utilized PtAu nanoparticles to concurrently improve the kinetics of ORR and OER in Li–O$_2$ batteries (Fig. 11(c)). Use of the bifunctional PtAu catalyst leads to high round-trip efficiency and decreased overvoltage. Since then, the use of metal catalysts in Li–O$_2$ batteries has increased considerably.

At present, the Li–O$_2$ battery is still in its initial stages, although many strategies have been investigated to overcome its issues. The cycle life and capacity of the Li–O$_2$ batteries currently being reported in many published papers are still far from being suitable for practical application. In the long term, increasing the fundamental understanding of the chemical and electrochemical reaction mechanisms in the cathode is the most important but most difficult task. Although Li–O$_2$ batteries have a long way to go before their use in practical applications, there is still hope for their development.

4. Conclusions and perspectives

Innovations in battery chemistry have significantly promoted and sustained the development of human society in terms of energy utilization. Advances in energy chemical engineering are what make innovation in battery chemistry possible, leading to the commercialization of rechargeable batteries. LIBs are an excellent example of the combination of battery chemistry innovation with energy chemical engineering. At present, the generation of renewable and clean energy is more conveniently and cheaply provided by the rapid development of solar energy and wind energy harvesting technologies. However, the utilization of intermittent sources of renewable energy must be combined with energy storage solutions. If further breakthroughs in energy storage systems can be achieved, they will promote sustainable development in numerous fields, both in the present and in the future, including the information industry, quality-of-life research, and the materials industry. Therefore, next-generation Li batteries are highly expected and under intensive research.

The battery chemistry, challenges, and recent advances in the energy chemical engineering of Li-ion, Li–S, and Li–O$_2$ batteries were briefly summarized in this review, providing a backdrop for the further development of next-generation Li batteries. Current strategies cannot completely solve the challenges presented by these batteries. More fundamental understanding and further developments in energy chemical engineering are required in the following areas:

(1) **Ion-transport mechanisms.** The current understanding of solid–solid and solid–liquid interfaces is still complex and vague, although some initial characterization tools and methods have been used to investigate the solvation/de-solvation of ions, interfacial formation reactions, and the ion-transport mechanism among multiple phases. Further in-depth investigations are required in order to consider the effect of the electric field and the complexity of the interface among multiple phases. Therefore, multiscale theories and experiments are imperative and will provide new understanding and guidance. For example, the utilization of density functional theory, molecular dynamics, spherical aberration electron microscopy, and synchrotron radiation will open up new avenues.

(2) **A stable interface on Li metal.** The Li anode is an indispensable part of a high-energy system. Understanding and regulating the interface on the Li anode is a key step toward feasible utilization of the Li anode. The introduction of a fluorinated interface holds promise in protecting the Li anode. The question of how to precisely regulate the components and structure of the SEI, which is not limited to the fluorinated interphase, is the key for further improving the coulombic efficiency of Li batteries. If a high coulombic efficiency of 70%–95% can be realized with a high areal current density (10 mA·cm^{-2}) and high areal capacity (> 6 mA·h·cm^{-2}), the practical application of the Li anode will be promising. Meanwhile, the introduction of a structured Li anode is an effective method. Here, achieving precise and uniform Li deposition in interconnected ionic and electronic channels is the key goal.

(3) **An intimate interface on the cathode.** For a full battery, the interface between the cathode and electrolyte is essential, but lacks current attention. Here, the transport of and reactions between ions and electrons are key issues. The question of how to construct stable electronic channels in a three-dimensional multiphase system that can tolerate volume change and high current density remains a challenge. The use of CNTs, graphene, and their hybrids contributes significantly to the formation of conducting networks. Regarding ion channels, resistance from the interface between the solid or liquid electrolyte is a problem. LiNbO$_3$ has been employed to suppress the space charge layer on certain cathode materials. To decrease interfacial resistance between the anode and solid electrolyte, the formation of an SEI by the introduction of film-formation agents to ensure good wettability is an emerging research direction.

(4) **Cooperation within full batteries.** Efficient cooperation among the anode, cathode, and electrolyte will greatly contribute to the stable operation of full batteries. Volume change, reaction heat, and the uniform distribution of ions and current densities at different depths of discharge should be considered when the match between an anode and a cathode is being designed. Chemical engineering may provide a more effective means of optimizing the parameters of batteries.

(5) **Battery safety.** Thermal runaway easily occurs when batteries are operated under uneven current density and short circuit. In such a situation, the SEI decomposes and the separator melts and shrinks, giving rise to further short circuit and increased temperatures. The cathode electrode then decomposes and releases a great deal of heat, leading to fire and even explosion. Initial material designs, heat-stable SEIs and separators, and current density have been explored in order to improve the safety of these batteries. In

addition, a battery management system is essential for safe batteries. Here, systems engineering within chemical engineering can play a part.

(6) **Battery application in smart electric vehicles.** Further optimization of batteries and materials in order to adapt the power supply behavior and usage features is necessary for the widespread commercialization of smart electric vehicles. The emerging self-heating technology in batteries satisfies the demands of electric vehicles by maintaining a constant temperature in the battery, which is a new direction.

(7) **The application of batteries in grid-scale energy storage systems.** There are many opportunities for rechargeable batteries to be employed in grid-scale energy storage systems. However, challenges also exist. Organic cathodes and sodium anodes, which are backed by a great deal of available resources, are very attractive for grid application, when the cost of energy storage is taken into account.

(8) **The popularization of next-generation Li batteries with new chemistry.** Innovations in business models, supply, and recycling chains are required to promote the popularization of next-generation Li batteries. A new business model would provide solid support to improvements in next-generation Li batteries, such as financial support, new instruments, and labor. It is also necessary to establish a resource supply and a battery recycling industry. Utilizing resources efficiently and recycling scrapped batteries are necessary for the sustainable development of next-generation Li batteries, and guidance from governments and market promotion will play important roles in these efforts.

Great progress has been achieved in Li-ion, Li–S, and Li–O$_2$ batteries during the past two decades. However, as yet, there is no ideal design that allows Li batteries to perform well under all conditions. Increasingly advanced characterization tools, advanced computer science, nanotechnology, and precision instruments provide new opportunities for the further development of batteries. In addition, persistent investigations into relevant science and technology are ongoing. This is the right time for the development of next-generation Li batteries in order to answer the challenges being presented by the world. The issues hindering Li batteries are being addressed with engineering, as discussed in this article. Through persistent engineering efforts, next-generation Li batteries will become the cornerstone of the future and will promote the sustainable development of human civilization.

Acknowledgements

Compliance with ethics guidelines

Xue-Qiang Zhang, Chen-Zi Zhao, Jia-Qi Huang, and Qiang Zhang declare that they have no conflict of interest or financial conflicts to disclose.

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