Solid electrolyte interphase on anodes in rechargeable lithium batteries

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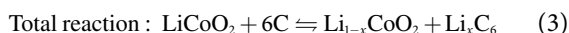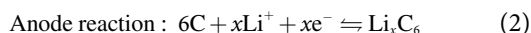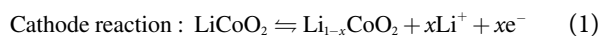
ABSTRACT

Highly safe and efficient rechargeable lithium batteries have become an indispensable component of the intelligent society powering smart electronics and electric vehicles. This review summarizes the formation principle, chemical compositions, and theoretical models of the solid electrolyte interphase (SEI) on the anode in the lithium battery, involving the functions and influences of the electroactive materials. The discrepancies of the SEI on different kinds of anode materials, as well as the choice and design of the electrolytes are detailedly clarified. Furthermore, the design strategies to obtain a stable and efficient SEI are outlined and discussed. Last but not least, the challenges and perspectives of artificial SEI technology are briefly proposed for the development of high-efficiency batteries in practice.

KEYWORDS

solid electrolyte interphase (SEI), lithium batteries, anode materials, electrolyte, dendrite

1   Introduction

Intensive environmental issues and extensive renewable energy harvest boost a massive demand for energy storage systems in modern sustainable society. Lithium battery, one of the reliable energy storage systems, has been widely used in intelligent electronics, electric vehicles, and stationary grids as well, owing to its high energy density, affordable cost, and long lifespan [1, 2]. However, lithium ion batteries (LIBs) still suffer from severe safety issues, due to the high chemical activity of Li, the volume change of anodes during the charge–discharge process, as well as the flammable organic electrolyte used in the LIB system. The working mechanism of LIB system (take $LiCoO_2$ and graphite as cathode and anode, respectively) can be illustrated in Fig. 1 and its relevant chemical reaction in the electrodes is described in Eqs. (1)–(3) [3, 4]

$$\text{Cathode reaction}: \ LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^- \qquad (1)$$

$$\text{Anode reaction}: \ 6C + xLi^+ + xe^- \rightleftharpoons Li_xC_6 \qquad (2)$$

$$\text{Total reaction}: \ LiCoO_2 + 6C \rightleftharpoons Li_{1-x}CoO_2 + Li_xC_6 \qquad (3)$$

In LIBs system, side reactions will be occurred at the interface of electrolyte and electrodes due to their high chemical and electrochemical activity. At the interface of anode material and electrolyte, solid electrolyte interphase (SEI) films arise at the solid–liquid interface during the first charge–discharge process [5, 6]. Similarly, cathode electrolyte interphase (CEI) films arise from the side reaction between the cathode material and the electrolyte. Although both SEI and CEI films play an important role in improving the cyclic stability, Coulombic efficiency, rate capabilities and safety, SEI film is more crucial and complicated than CEI films. This should be attributed to the diversity of anode materials, resulting in the complicated composition of SEI film. Besides, lithium dendrite is usually generated on the surface of anodes, leading to the failure of battery. Thus, stable SEI film can restrain the wretched lithium dendrite and enhance the cyclic stability. However, the formation of SEI film also consumes a part of lithium ions in the first cycle, which is an irreversible reaction, making a capacity loss and decreasing the Coulombic efficiency of battery. In the past few years, scientists and researchers usually considered that SEI film just existed in the organic electrolyte by preventing the solvent molecules from passing, serving as a passivation layer and suppressing the further side reactions. However, in recent years, SEI can also be generated in aqueous systems, broadening the cognization of SEI film. For instance, Suo's research successfully confirmed the formation of the SEI in an aqueous system by altering the lithium ion solvation sheath structure with super concentration. This innovative "water-in-salt" electrolyte (WiSE) highly expands the electrochemical stability window [7]. Additionally, WiSE not only makes it possible to construct a series of high voltage/energy-density aqueous LIB with unprecedented safety but also brings high flexibility and even "open configurations" that have been hitherto unavailable for any LIB chemistry [8].

As is known to all, electrochemical stability window and thermodynamic stability significantly affect LIB with high energy density. Based on an open-circuit potential state, the energy separation between the lowest vacancy molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the
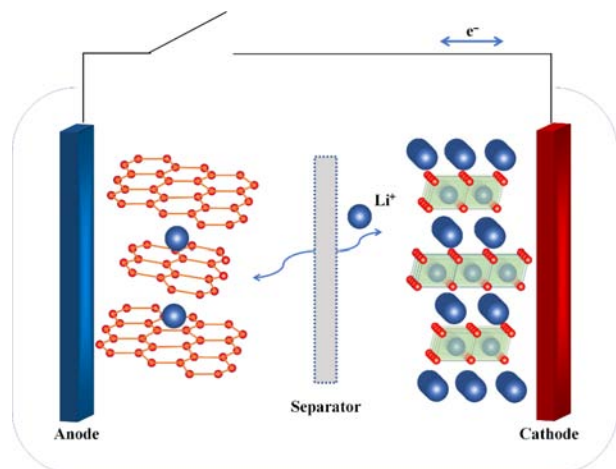
Figure 1 Schematic illustration of working mechanism based on LiCoO₂ and graphite battery. It comprises a cathode and an anode separated by a separator film. An electrolyte serves as the medium to transport lithium ion when the battery is under operation.

electrolyte is the "window" of the electrolyte (Fig. 2) [9]. These two electrodes are electronic conductors with their chemical potentials μ_A and μ_C. The μ_A of the anode above the LUMO will reduce the electrolyte unless the passivation layer blocks the electron transfer from the anode to the electrolyte LUMO. On the contrary, the cathode below the HOMO will oxidize the electrolyte unless the passivation layer prevents electrons from the electrolyte HOMO to the transmission of the cathode. Therefore, thermodynamic stability requires that the electrode electrochemical potential μ_A and μ_C be positioned within the electrolyte window, limiting the open-circuit voltage (V_{oc}) of the battery to be less than E_g. A passivating SEI layer can give kinetic stability to a larger V_{oc}, provided that ($eV_{oc} - E_g$) is not too large.

Therefore, to ensure excellent electrochemical performance, uniform thickness and chemical composition of SEI with both mechanically stable and flexible are significant [10–13]. Thus, many strategies have been proposed to establish homogeneous and stable SEI, such as surface modifications of electrode materials as well as explorations of electrolytes and their corresponding additives [14]. For instance, strategies by optimizing the composition and structure of electrode materials can efficiently alleviate the SEI rupture caused by the huge expansion of the electrode during the repeated charge–discharge process. Besides, strategies by modifying the electrolyte compositions (solvents, lithium salts, and electrolyte additives) can availably generate stable, self-healing, uniform, or mechanically strong SEI film.
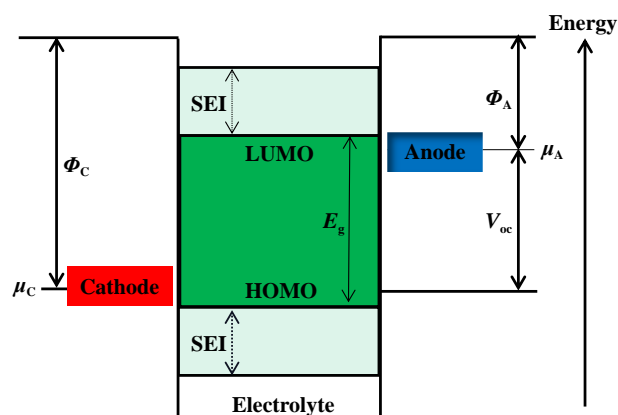

Figure 2 Schematic of the energy diagram for a battery. Φ_A and Φ_C are the work functions of anode and cathode, respectively. E_g is the electrochemical stability window of electrolytes. μ_A and μ_C are the redox potential of the anode and cathode, respectively.

Furthermore, artificial SEI strategies, by elaborately designing the morphology and structure of SEI film, can realize the directional control of the SEI film, reducing electrolyte loss during the cycles. Although the above strategies and research highly strengthened the electrochemical and mechanical stability, a more efficient and stable SEI film is greatly needed. Besides, the formation and evolution mechanism of SEI film is still not profound enough. For example, the discrepancies of SEI formation and evolution on different types of anode materials, the effects of different kinds of electrolytes on the composition of SEI, and selecting anode materials and electrolytes to obtain SEI film with chemical and mechanical stability need to be further studied.

In this review, we first summarized the latest studies about SEI film in lithium batteries, such as the SEI formation mechanism and relevant theoretical models, as well as the discrepancies of SEI film on different types of anode materials. Besides, the influence of various electrolytes on the structural and compositional properties of SEI film was reviewed. Subsequently, we discussed the possible formation and evolution mechanism of SEI film during the repeated charge–discharge process in the LIB system. Furthermore, the possible transport mechanism of lithium ion in various SEI film was systematically discussed. At last, the challenges and perspectives of artificial SEI technology were briefly proposed for the development of high-efficiency batteries in practice, and we focused on designing and preparing a chemically and mechanically stable SEI between the electrode materials and electrolytes to improve battery performance.

2 SEI formation and models

In the anode, organic solvents are decomposed at different potentials on the surface of an electrode, generating various radicals or ions and subsequently leading to a consecutive reaction to form a plurality of compounds [15, 16]. These compounds have a high concentration on the electrode surface and gradually construct into an organic/inorganic hybrid layer [17, 18]. At the early stage of SEI formation, the insoluble compounds preferentially deposit on the electrode sites due to the high surface energy, resulting in an island-like growth. Besides, this process will also be affected by the geometry of the exposed surface and the initial deposited surface of the SEI film [19]. In the growth stage, cumulative SEI growth is a dynamic process [20]. Due to the gradually exposed surface of the anode, SEI film more easily covers the electrode surface unevenly and thickly, which exceeds the electron tunneling distance [21]. The possible chemical reactions of the metal lithium electrode surface during the SEI film formation have been widely studied [22]. So far, research of SEI on anode has gone through a long process. The passivation layer on lithium metal was first observed by Dey et al. in 1970 [23]. Later, in 1979, Peled introduced the concept of SEI [5]. Peled further proposed a bilayer structure for SEI in 1983, consisting of a dense thin inner layer and a thick porous outer layer [24]. In 1985, Nazri et al. identified the presence of Li₂CO₃ and polymers in SEI by infrared (IR), secondary ion mass spectrometry (SIMS), and *in situ* X-ray diffraction (XRD) [25]. In 1987, Aurbach et al. confirmed the presence of lithium alkyl carbonate salts in SEI using IR and X-ray photoelectron spectroscopy (XPS) [26]. In 1990, Fong et al. confirmed the SEI layer on graphite [27]. In 1995, Kanamura et al. further characterized LiF and many organic components in SEI formed in LiBF₄ salt-based electrolytes using XPS [28]. In 1997, Peled et al. pictured SEI as a mosaic structure [29]. In 1999, Aurbach et al illustrated the formation process of SEI starting from electrolyte reduction on the electrode surface [30]. In 2004, Christensen et al. proposed physics-based continuum models that were developed to simulate SEI growth, assuming SEI is mainly

Li_2CO_3 [31]. In 2006, Edström et al. proposed a schematic picture of the SEI on a graphite particle [32]. In 2012, Shi et al. calculated the lithium ion diffusion in Li_2CO_3 via a knock-off mechanism and together with the porous organic layer, and they proposed the two-layer/two-mechanism model [33]. In 2014, Zheng et al. first visualized the three-dimensional (3D) multi-layered structures and the mechanical properties of the SEI formed on a silicon anode material for next generation lithium ion batteries using a scanning force spectroscopy method [34]. In 2017, Prof. Cui and his co-workers explained the SEI model at atomic resolution by using cryo-electron microscopy for the first time. They proposed two nanostructures (inlay and multilayer) formed on the surface of lithium metal anode in commercial electrolytes with fluorine additives [35]. This has made a great contribution to future research work. In 2019, Hou et al. used mass-sensitive scanning transmission electron microscopy to observe the evolution of SEI film [36]. The evolution of anode SEI knowledge and models over the past 40 years is shown in Fig. 3 below.

In order to better understand the formation and composition of SEI film, researchers have proposed different SEI structural models. There are mainly two models for the SEI film now, the mosaic model (composed of randomly distributed inorganic and organic parts) and the multilayer model (composited of internal inorganic layers and external organic layers), as shown in Fig. 4. Mosaic model indicates that SEI film is a mixture of insoluble multiphase products deposited on the surface of the anode. The conduction mechanism of lithium ions in SEI is realized through vacancies and interstitial lattice defects. Particularly, the conductivity of lithium ions at the grain boundary is much higher than that of the bulk phase due to the high concentration of lithium ions, which is easier to aggregate at the grain boundary [37, 38]. Besides, the inhomogeneous distribution of SEI components will lead to inconsistent transport paths for lithium

ions, and the fastest way to transmit lithium ions is prioritized [39]. This causes stress concentration in the process of lithium deposition, resulting in the uneven plating-stripping of lithium in the lithium metal anode, further leading to the formation of lithium dendrites as well as " dead Li" [2, 40]. By studying the diffusion mechanism of lithium ions on the inorganic components at the solid electrolyte interface, it was found that the dominant diffusion pathway for Li ions on the SEI layers is the LiF surface due to the relatively lower energy barriers and larger diffusion coefficients [38]. The study of these micromechanisms is helpful in reasonably designing the composition selection of artificial SEI layers and improving the performance of lithium batteries.

Multilayer model demonstrates that SEI is expressed as an independent layer with two or more layers with different structural properties [30]. The inner layer is thin and compact, and the second layer at the top is a more porous and structured opening. Prof. Aurbach and his co-workers conducted in-depth electrochemical and spectroscopic studies on carbon electrodes in lithium battery systems. They proposed a multilayer SEI structure based on X-ray photoelectron spectroscopy measurement. Unlike the mosaic SEI model, the layered SEI has a more regular distribution in composition. The inner layer is in a low oxidation state with an inorganic substance, and the outer layer is in a high oxidation state with an organic layer [22]. The preferential distribution of these organic/inorganic species is related to the electrolyte composition. Besides, the chemical distribution of multilayered SEI is more homogeneous than that of mosaic SEI, which has the advantage of ion transport. The uniform ion flux and electric field can further avoid the generation of "dead Li" and local stripping of lithium [41].

Both the mosaic model structure and multilayer model structure depend on the specific solvent and lithium salt
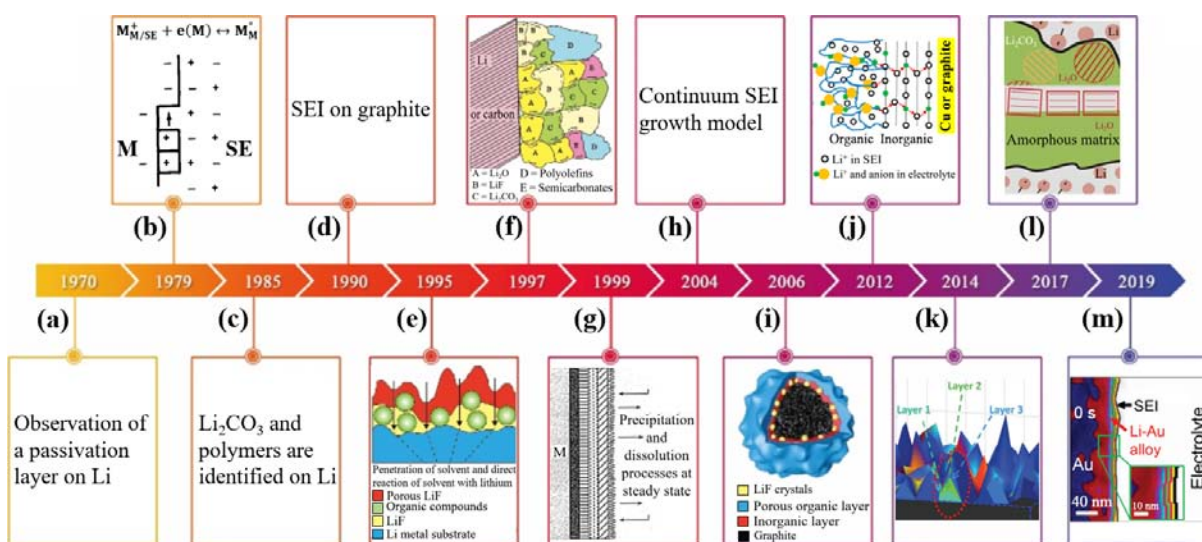

Figure 3 Evolution of knowledge and models of SEI on anode in the past four decades. (a) In 1970 [23], Dey first observed the passivation layer on lithium metal. (b) In 1979, Peled introduced the concept of SEI. Reproduced with permission from Ref. [5], © The Electrochemical Society 1979. (c) In 1985 [25], Nazri and Muller identified Li_2CO_3 as one of the main components in SEI. (d) In 1990 [27], the SEI layer on graphite was confirmed. (e) In 1995, the components of SEI were analyzed with XPS. Reproduced with permission from Ref. [28], © The Electrochemical Society 1995. (f) In 1997, Peled pictured SEI as a mosaic structure. Reproduced with permission from Ref. [29], © The Electrochemical Society 1997. (g) In 1999, Aurbach et al. illustrated the formation process of SEI starting from electrolyte reduction on electrode surface. Reproduced with permission from Ref. [30], © Elsevier Science S.A. 1999. (h) In 2004 [31], physics-based continuum models were developed to simulate SEI growth, assuming SEI is mainly Li_2CO_3. (i) In 2006, Edström et al. proposed a schematic picture of the SEI on a graphite particle. Reproduced with permission from Ref. [32], © Elsevier B.V. 2005. (j) In 2012, Shi calculated the lithium ion diffusion in Li_2CO_3 via a "knock-off" mechanism and, together with the porous organic layer, they proposed the two-layer/two-mechanism model. Reproduced with permission from Ref. [33], © American Chemical Society 2012. (k) In 2014, Zheng revealed the structural diagram of SEI. Reproduced with permission from Ref. [34], © the Owner Societies 2014. (l) In 2017, Prof. Cui and his co-workers explained the SEI model at atomic resolution by using cryo-electron microscopy for the first time. They proposed two nanostructures (inlay and multilayer) formed on the surface of lithium metal anode in commercial electrolytes with fluorine additives. Reproduced with permission from Ref. [35], © Li, Y. Z. et al. some rights reserved; exclusive licensee American Association for the Advancement of Science. (m) In 2019, Hou et al. used mass-sensitive scanning transmission electron microscopy to observe the evolution of SEI film. Reproduced with permission from Ref. [36], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.
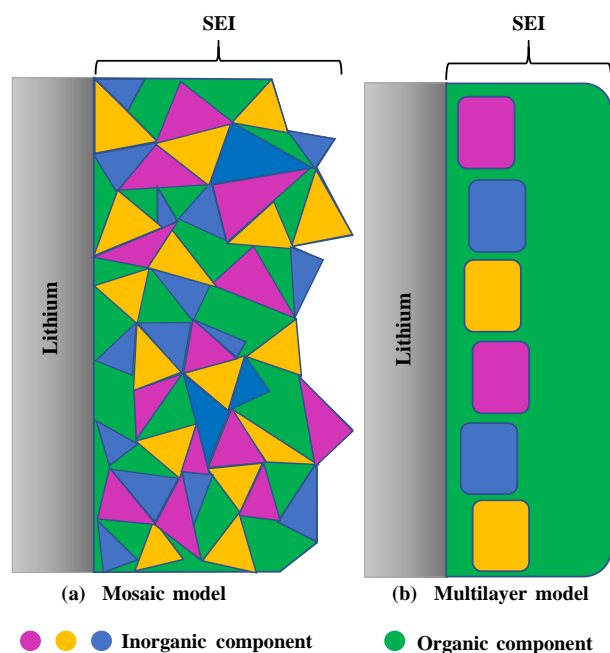
Figure 4 Schematic diagram of the two models of SEI: (a) The inhomogeneous distribution of SEI components will lead to inconsistent lithium ion transmission paths, and lithium ion is transmitted in the fastest way first. (b) The layered SEI has a more regular distribution. The inner layer is a low oxidation state inorganic substance, and the outer layer is a high oxidation state organic layer.

Figure 5 The SEI can be divided into two parts: an inner SEI and an outer SEI. The inner SEI is continuous, dense, and impermeable to electrolytes, most probably composed of Li_2O. The outer SEI is mainly composed of loose organic oligomers that result from the degradation of solvent molecules. The free outer SEI is permeable to electrolytes.

composition. At the same time, when the anode surface is treated, the corresponding SEI structure composition will also be changed [42]. The chemical profile has been established by *in situ* liquid-SIMS technique, which reveals the structure of SEI (as shown in Fig. 5) [43]. The structure of SEI consists of two layers, where the inner layer is dense inorganic and the outer layer is rich in organic matter, which has diffusion and permeability to the overall electrolyte. When lithium ions migrate or leave the dense part of the SEI, the existence of this diffused SEI layer may act as an intermediate phase. Due to the solvent molecules are not allowed in the dense part of the SEI, the original solvated sheath must be stripped. The oxygen-rich functional groups in the porous outer layer can provide sufficient lithium ions coordination. Therefore, the solvation environment of the lithium ions will not suddenly change when migrating from the electrolyte to the inner inorganic layer through the outer layer, as the coordination points in the outer layer have gradually altered the solvation environment. Cheng [44] pointed out that the layered model and the mosaic model are not contradictory because the building blocks in each layer of the layered model are still distributed in the form of a mosaic. The latest research shows that the electrode potential of the anode dominates the evolution of SEI structure. The anode potential determines the reduction products in the electrolyte, when the electrode potential is low, the SEI exhibits a bilayer structure. Accordingly, when the electrode potential is high, the SEI exhibits a mosaic structure [45]. This provides rational guidance to regulate the structure of SEI. In addition to the above two mainstream SEI models, with the development of cryo-electron microscopy technology in recent years, the SEI structure was observed under cryogenic transmission electron microscopy (cryo-TEM) which is similar to the "plum pudding model", where the amorphous phase resembles the pudding and the embedded crystalline microphases resemble plums [42, 46].

The formation of SEI is a pretty complicated process. Researchers have made a lot of efforts in the mechanism of SEI formation with experimental and computational routes, which
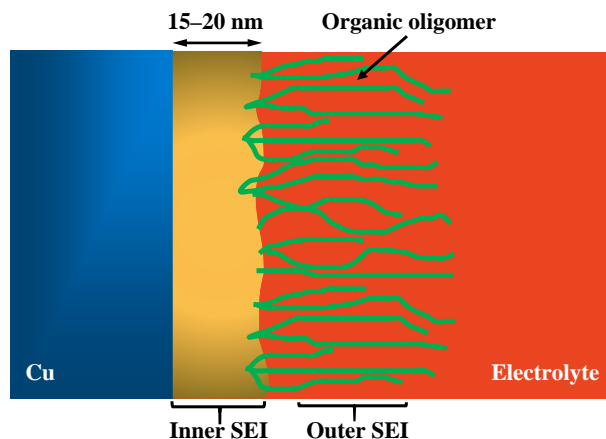
have made significant progress in understanding the electrochemical process of SEI formation. However, the explanation of the mechanism is still controversial, and no impeccable model can accurately demonstrate the behavior of electrode material and electrolytes during the formation of layers. But the materials of the electrode and electrolyte composition are the key factors affecting SEI, so that we will discuss the impact of SEI from the viewpoint of the varieties of electrode materials and electrolytes.

3 SEI discrepancies on different-type of anode materials

Anode materials can be categorized into three types based on their working mechanisms: intercalation-type, alloying-type, and conversion-type. Additionally, lithium-based metal anodes will be discussed at the end. The interaction between the electrolyte and the various types of electrode materials is different, especially the role of the SEI. For example, the intercalation-type materials represented by graphite have a low voltage platform and the potential is close to the LUMO of most solvents, resulting in the reduction reaction of electrolyte and the formation of SEI. During the repeated charge–discharge process, the solvent molecules can intercalate into the layered materials and give rise to the exfoliation of graphite. Differently, the alloying-type materials have a higher capacity than those of intercalation-type materials due to the formation of an alloy between anode materials and lithium during the charge and discharge process. However, the enormous volume changes generated in the alloying–dealloying process result in the destruction of SEI film. Conversion-type materials have a higher specific capacity and a more stable material structure. In the process of charge–discharge, transition metal oxides undergo multi-electron reversible redox reactions with lithium ions through the conversion reaction mechanism. SEI on conversion materials will contribute an extra capacity because of its reversibility. Thus, the SEI formation and functions of different-type electrode materials will be discussed in the following sections.

3.1 Intercalation-type materials

Active sites in intercalation materials store the energetic ions, and the chemical redox potential is one of the critical parameters, which can influence the formation of SEI. Graphite, as one of the most common intercalation anode materials in LIB, presents a low voltage platform (~ 0.05 V vs. Li$^+$/Li) and a theoretical capacity of

~ 372 mAh·g⁻¹ [47, 48]. This low potential is close to the LUMO of most solvents, resulting in the electrolyte reduction to form an SEI layer. The process of SEI formation on the graphite surface is shown in Fig. 6. Lithium and organic solvents are intercalated into the graphite interlayers during the charge–discharge process, in which the organic solvents are further decomposed, causing the graphite layer to fall off gradually [49, 50]. The reaction between the chemicals generates the SEI layer and H_2O, which accelerates the decomposition of salt. This further changes the composition of the SEI layer and distorts the SEI structure. The ineffective SEI layer is a source of solvated lithium ions captured in the growth layer, which can lead to the formation of metallic lithium clusters [51]. The solvated lithium ions trapped in the growing SEI react with the electrolyte to increase the reduction species surface concentration and significantly increase charge transfer resistance. The accumulated reduction species on the graphite surface decrease the pore size in the SEI layer, leading to sluggish lithium ion intercalation/deintercalation kinetics. The solid and effective SEI layer can prevent further solvolysis and solvent co-intercalation, preventing the graphite layer from peeling off and improving cycle efficiency. In addition, the effective SEI layer will significantly reduce the double layer capacitance and increase the ionic conductivity in the electrode/electrolyte interface compared with the invalid SEI layer.

Numerous studies have shown that modifying graphite through physical or chemical methods can reduce the irreversible capacity loss. To better play the role of effective SEI and inhibit the generation of ineffective SEI, a passivation layer can be prepared on the surface of the graphite material. For instance, natural graphite (NG) can be coated with pyrolytic carbon to form a uniform coating on its surface, which leads to the formation of a thin and compact SEI film on the outer surface of the coated NG spheres, and inhibits the formation of internal SEI film around internal cracks, resulting in significantly enhanced electrochemical performance [52]. Yu et al. prepared a kind of metallic nickel nano-composite particle coating that effectively suppresses the intercalation of lithium solvation in graphite, minimizing the exfoliation of the graphene layers [53]. Besides, zirconia coating on graphite was examined to enhance the cycling stability of the graphite anodes in Li-ion batteries, the combination of nanocrystalline-zirconia, and the *in situ* formed surface films better protects graphite from destruction upon cycling, thereby improving the rate performance and cycle stability of the electrode materials [54]. Polydopamine (PD) can be uniformly coated on the surface of graphite particles as an artificial solid electrolyte interface layer to prevent the direct contact between electrolyte and graphite surface and improve the rate performance and recy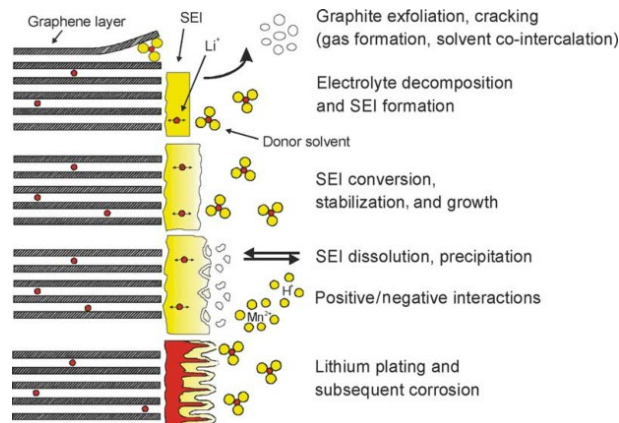clability of graphite anode electrodes by forming an ion conduction path for lithium ions [55]. The PD-coated graphite electrode showed higher capacity retention and lower resistance compared to graphite because of the high stability of PD as an artificial SEI layer. Besides, the graphite surface can also be coated with a layer of $Li_4Ti_5O_{12}$ (LTO) by the sol-gel method [56], and the zero-strain material LTO acts as the artificial SEI to suppress the decomposed electrolyte and solvent co-intercalation, improving the structural stability of the graphite. Compared with the original graphite, the rapid lithium ion transfer of the LTO coating makes the LTO-coated graphite more kinetically advantageous. The graphite is exposed to lithium vapor to form a stable Li_2CO_3 passivation layer on the surface of the graphite material. The passivation layer acts as a preformed SEI and protects electrolytes from the decomposition and regeneration of SEI film [57].

In addition to being used as a surface coating for graphite anodes, spinel LTO itself, with a theoretical capacity of 175 mAh·g⁻¹, is also another classic anode material. The charge/discharge voltage plateau of LTO is about 1.5 V, which is higher than the decomposition voltage of most of electrolytes. But, this does not prevent the formation of SEI on the surface of LTO. Most of the SEI dissolves during the subsequent discharge process along with the accumulation of residual SEI [58]. The LTO anode with carbon as the conductive agent is affected by SEI accumulation at high temperatures, and the cycle performance is degraded. Therefore, preparing a carbon-free LTO electrode is an effective solution to solve the high-temperature cycle characteristics of LTO. Huang proposed a new experimental model. They prepared binder and conductive additive-free LTO thin-film electrodes and introduced Al-ZnO (AZO) surface coatings to manipulate LTO electrode–electrolyte interfacial properties. They found that the electrochemical reaction between Li and AZO during initial discharge/charge process generates an efficient and high performance artificial SEI protection layer. This artificial inorganic SEI layer has high ionic conductivity, protecting the electrode surface from electrolyte decomposition, and therefore dramatically improving the cycling and rate performance of the LTO anode [59]. This provides an important idea for in-depth understanding of the enhancement mechanism of electrode surface coating of the battery, so as to determine their interfacial chemistry and phase transition during the intercalation/deintercalation.

Recent studies have reported that reducing the charge/discharge voltage of LTO to 0 V can increase its specific capacity and rate discharge performance without affecting its cycle performance [60, 61]. However, when the voltage drops below 1 V, most of the electrolyte begins to decompose, leading to the formation of SEI film on the surface of the material. To address this issue, He et al. [62] prepared carbon-coated LTO and found that the reductive decomposition of the electrolyte occurred at 0.7 V only in the first cycle in the carbon-coated LTO material, while SEI continued to form on the uncoated LTO. The carbon coating on the surface of LTO covers the active sites, reducing the continuous reduction and decomposition of electrolytes. The main component of SEI mainly depends on voltage, and its formation on LTO is affected by electrode morphology and surface area. Regularly shaped materials with a small specific surface area form an SEI after a long cycle, while irregularly shaped materials with a large specific surface area form an SEI after several cycles. Therefore, adjusting the morphology of the LTO material and the cyclic voltage range can help control the formation of the SEI, and improve the performance of the LTO-based lithium battery.

In the intercalation/deintercalation mechanism, for most materials, whether graphite anode or other anode materials, the preparation of passivation layer coating is a common method to reduce the negative impact of the SEI layer. Of course, the study of

Figure 6 Schematic diagram of the process of forming SEI on the graphite surface. Reproduced with permission from Ref. [51], © Elsevier B.V. 2005.

SEI on intercalated anode materials needs to be further studied in order to understand the formation mechanism of SEI deeply.

3.2 Alloying-type materials

The alloying/dealloying mechanism means that the active material forms an alloy with lithium ions during the charge–discharge process. According to this mechanism, for instance, in the Silicon (Si) or Tin (Sn) anode, each Si or Sn atom can react with 4.4 Li atoms, forming $Li_{4.4}Si$ or $Li_{4.4}Sn$ alloy with a high capacity of 4200 and 990 mAh·g^{-1}, respectively.

$$M + 4.4Li \leftrightharpoons Li_{4.4}M \ (M = Si, \ Sn) \qquad (4)$$
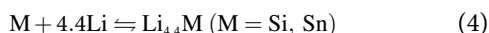
Si-based materials are promising anode materials for the next-generation rechargeable lithium batteries because of their high theoretical capacity and low charge-discharge potential (~ 0.4 V vs. Li/Li$^+$). However, the Si anode materials suffer from substantial volume change (300%–400%) [63, 64], leading to severe pulverization and detachment from the current collector. Moreover, the SEI film does not have mechanical tolerance to endure the massive volumetric changes during the expansion/contraction of the silicon surface. As a result, the electrolyte decomposes continuously to cover the newly exposed surface and increase the thickness of the SEI film, leading to the increase of SEI film resistance. This process results in a continuous decrease in the reversible capacity of cycling. In order to improve the performance of alloy anode materials, John et al. studied the degradation mechanism of nanoporous alloy lithium ion batteries and proposed strategies by reducing fragmentation in the lithiation process and improving the mechanical stability of SEI in the delithiation process [65].

To overcome various problems of the Si anode in circulation, LiF was coated on the surface of silicon by spray drying to form an artificial SEI film [66]. This LiF-based artificial SEI film can prevent Si from reacting with the electrolyte and enhance the structural and interface stability. Thus, the capacity retention of Si can be significantly increased, and the side reaction and the capacity loss in the first cycle are reduced [67]. With 5–10 atomic layers of alumina atomic layer deposition (ALD) coating, the thin film silicon electrode can deliver a 2600 mAh·g^{-1} capacity. The ALD coating can act as an artificial SEI layers, which can improve the cycle stability and facilitate the charge transfer at the Si electrode surface. In addition, the thickness of artificial SEI film is also an important factor affecting the performance of the Si anode [68]. Thus, lithium phosphorus oxynitride (LiPON) and its relevant artificial SEI film with different thicknesses were prepared for further research [69, 70]. The LiPON layer can control the volume expansion of the material during cycling to improve the mechanical stability of Si, but LiPON will reduce the performance of the battery at high rates. Moreover, it was found that 40–50 nm is the critical thickness for the LiPON-based artificial SEI film. When the thickness is greater than the critical thickness, the synthetic SEI film dramatically reduces the decomposition and irreversible capacity of the electrolyte [70].

In addition to building a protective layer, Jiang et al. used soft nylon fabric modified by a conductive Cu-Ni transition layer as artificial SEI. This structure has high conductivity and flexibility, which can improve the mechanical stability of silicon anode and the cycling performance of battery [71]. This provides an effective approach to enhance the structural stability of silicon anode, which can also be applied to other alloying anodes with similar volume change issues. In addition, the multilayer graphene can protect the nano-Si particles from direct exposure to the electrolyte, which is beneficial to maintain the stability of the SEI [72]. Besides, the electrostatic electrospinning method was used to encapsulate Si nanoparticles into hollow carbon tubes, while the

voids around the Si nanoparticles could relieve the expansion of the silicon and prevent the rupture of the electrode. Furthermore, hollow carbon tubes can avoid silicon exposure in the electrolyte and form a stable and thin SEI film [73]. Similarly, the "double shell" dual carbon shells were used to encapsulate silicon volume change, which was proposed to solve the enormous volume change and the severe smash caused by the unstable SEI layer. The inner carbon shell provides limited internal voids so that the internal carbon shell can buffer the size of silicon nanoparticles. In contrast, the static shell is not only conducive to the formation of stable SEI film but also can reduce the volume expansion of the electrode [74].

Besides, the design of the electrolyte system can also effectively alleviate the impact of the silicon volume expansion during the cycle. The current commonly used electrolyte can cause the electrode to form an organic-inorganic SEI during the cycle, which is tightly combined with the surface of the alloy anode. As shown in Fig. 7 , tight combining will cause similar high deformation of SEI and alloy, resulting in the broken and reformation of SEI. The alloy anode will be pulverized and isolated [75]. If a strong SEI with low adhesion (high interface energy (E_{int})) is formed on the surface of the alloy anode, the alloy can be repositioned at the interface to adapt to the huge volume changes [76].

3.3 Conversion-type materials

The transition metal oxides will undergo a multi-electron reversible redox reaction with lithium ions through a conversion reaction mechanism, which can act as the electrode materials for conventional lithium ion batteries to store lithium. Several pure transition metal compounds, such as oxides, fluorides, sulfides, and phosphides, were also able to undergo conversion reactions with lithium ions [77, 78]. The general formula of the conversion reaction can be expressed as

$$mnLi^+ + M_nX_m + mne^- \leftrightharpoons mLi_nX + nM \ (M = transition \ metals) \qquad (5)$$
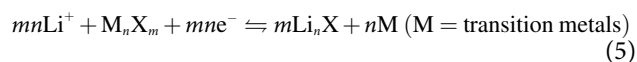
The low Coulombic efficiency of transition metal compounds is partly due to the drastic volume change that causes the material to be pulverized and powdered during the charge/discharge process [79, 80]. The side reaction of the electrolyte decomposes on the surface of the transition metal compound particles during the first discharge, resulting in a passivation film (SEI film) on the surface of the particles. Since this side reaction process consumes a certain amount of lithium ions, the formation of SEI film contributes a certain irreversible capacity. However, Tarascon found extra capacity in the CoO/Li [81, 82] half-cell and speculated that the additional capacity was related to the polymer gel-like reversible film formed by electrolyte degradation. As shown in Fig. 8, when Cu_3N was electrochemically reduced by Li, it decomposed into Cu nanoparticles and Li_3N, and a polymer layer appeared at the same time [82]. This phenomenon is also confirmed in other transition metal oxides such as Fe_2O_3 or Fe_3O_4 [83], NiO [84, 85], CuO [86, 87], and MnO [72, 88].

The polymer gel-like layer formed by electrolyte decomposition has been speculated as the SEI layer [81]. Moreover, the SEI layer
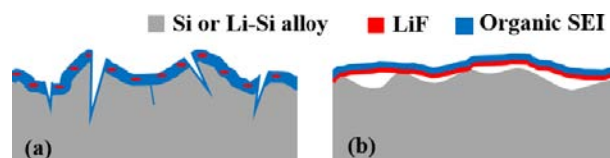

Figure 7 Schematic of the cycled alloy anode with (a) an organic, low E_{int}, and non-uniform and (b) an inorganic, high E_{int}, and uniform lithium alloy-SEI interface.
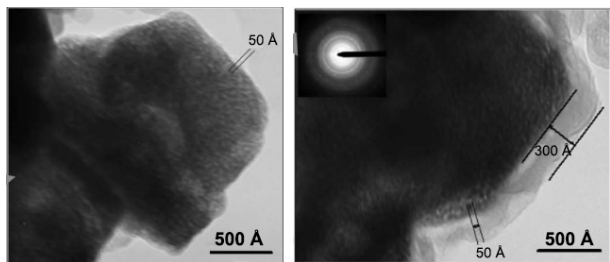
Figure 8 TEM image of a Cu₃N electrode in a Cu₃N/Li battery. The TEM image of a discharge sample shows its nanometer characteristics and the growth of the polymer layer. Reproduced with permission from Ref. [82], © Éditions scientifiques et médicales Elsevier SAS 2003.

Figure 9 Schematic diagram of SEI forming process on the surface of lithium metal.

can also provide excess lithium ion storage sites through pseudo-capacitance-type behavior [89, 90]. $Fe_3O_4/FeO/C$ [91] composites with a hollow structure and carbon shell were found that the extra capacity was related to the content of FeO, which means that FeO has a catalytic effect on the formation of the gelatinous film. In summary, extra capacity can be utilized when using a transition metal oxide material as an electrode. In future studies, researchers can explore suitable catalysts and temperatures for the SEI film to improve the cycle performance. In addition to studying anode materials of single transition metal oxide, Fang et al. used a conductive Al_2O_3/carbon layer derived from molecular layer deposition (MLD) to stabilize the structure of cactus-like $NiCo_2O_4$ nanocrystal (NC) anode. Al_2O_3/carbon buffer layer can prevent $NiCo_2O_4$ NCs agglomeration and form a stable SEI, which hinders the permeation of electrolytes and improves the cycle performance [92]. The design and introduction of MLD-derived hybrid coating may open a new way to conversion-type anode materials beyond $NiCo_2O_4$ to achieve high cyclability. The latest research shows that the composite materials of transition metal and its oxide can promote the reversible transformation of SEI film to improve the capacity [93]. This also provides a new strategy for the design of conversion anode materials.

3.4 Stripping/plating Li-metal

With the fast development of portable electronic devices and electric vehicles, graphite and other anode materials used in lithium ion batteries can no longer meet the requirement of high-energy-density and high-power-density. Therefore, lithium metal anodes have once again become one of the research hotspots due to their high theoretical capacity of 3860 mAh·g⁻¹ and the lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode) [94–97]. However, lithium metal anodes are highly reactive to liquid electrolytes due to the high chemical activity of metallic Li, leading to the LUMO level of all electrolytes being lower than the Fermi level of lithium metal. Therefore, SEI is more easily formed on the surface of the Li anode, which causes low Coulombic efficiency and limited cycle life [98].

As shown in Fig. 9, the heterogeneity of SEI highly affects the formation of lithium dendrites [99]. The physical characteristics of SEI play a vital role in the nucleation and growth of Li, resulting in different types of lithium dendrites, such as mossy, whisker, and nodule-like Li. The growth of lithium dendrites will further destroy the fragile SEI due to the vast stress generated on the surface of Li. There are mainly two strategies for regulating the SEI layer on Li metal anode, such as using functional electrolyte additives or fabricating a mechanically robust protective layer (or artificial SEI). These strategies not only homogenize the Li ion flux and electric field but also restrain the enormous stress generated on the surface of Li metal, obtaining dendrite-free Li metal anodes.

Building a protective layer on the lithium metal anode is one of the most effective practical approaches to stabilize lithium metal
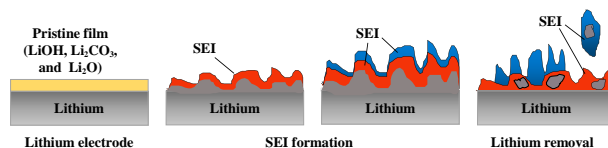
anode interfaces. Inorganic protective layers, such as Li_3PO_4 [100], Li_3N [101], tetraethoxysilane, or Al_2O_3 [102], are applied to lithium metal anodes. Polymers with superior electronically insulating properties, self-healing properties, and flexibility to accommodate volume changes are considered suitable protective layers. Various polymers, such as polyacetylene [103], tetraethoxysilane [104], have demonstrated anode protection. Xiong et al. synthesized a binder and self curing supramolecular copolymer LiPEO-UPy as artificial organic SEI of lithium anode. This LiPEO-UPy@Li anode can eliminate the formation of lithium dendrite and improve the cycling performance [105]. Song et al. designed a lithiophilic matrix with a 3D Li structure coated with polyacrylic acid (PAA) as an artificial SEI. LiPAA thin film can inhibit the formation of Li dendrite and effectively promote the transfer of Li⁺ [106]. Meng et al. *in situ* prepared covalent organic framework (COF) films as artificial SEI, which suppressed the significant volume change of the anode [107]. Admittedly, whether it is an inorganic or organic protective layer, these artificial SEI layers are effective to some extent in suppressing side reactions, alleviating volume expansion and Li dendrite formation. Furthermore, the electrochemical performances can be dramatically improved, demonstrating artificial SEI as a promising way to tackle the issues of lithium metal anode.

Besides, there are still some protective layers except the above mentioned. For example, introducing silver nanoparticle modification to form Li-Ag-LiF surface can obtain lithium metal batteries (LMBs) with high performance. A robust polydopamine-Cu ion (PDA-Cu²⁺) [108] coating layer formed by the aggregation of nanoparticles can regulate and guide the lithium metal growth. A trace amount of lithium nitrate ($LiNO_3$) and copper fluoride (CuF_2) was employed in electrolytes to build robust electric double layer structures on a lithium metal surface, and the stability of SEI was obviously improved. The modified lithium metal electrode can achieve an average Coulombic efficiency of 99.5% over 500 cycles, enabling a long lifespan and high capacity retention of practical rechargeable batteries [109]. Moreover, the coating layer interacting with copper ions can significantly promote the fast diffusion of lithium ions and induce the formation of a stable SEI layer. Besides, an SEI layer on lithium metal sputtered by graphite-SiO_2 [110] can achieve uniform lithium deposition without dendrites, resulting in stable voltage distribution and excellent long-term cycling.

In general, whether through the use of functional electrolyte additives or the manufacture of mechanically robust protective coatings, in order to improve the performance of lithium metal batteries, the SEI layer should possess the following characteristics: (1) high ionic conductivity for fast lithium ion transport, (2) electronic insulation/low electric conductivity for inhibiting electrolyte decomposition, (3) good mechanical strength to prevent dendrite penetration, and (4) high chemical stability to endure long-term cycling processes.

In addition, the structure of the SEI film in LMBs is related to the composition of the electrolyte. As shown in Fig. 10 [111, 112], the SEI formed by electrolytes and their additives has been systematically studied. The SEI developed in the widely used carbonate-based electrolyte ethylene carbonate-diethyl carbonate (EC-DEC) contains small crystal domains and it was randomly
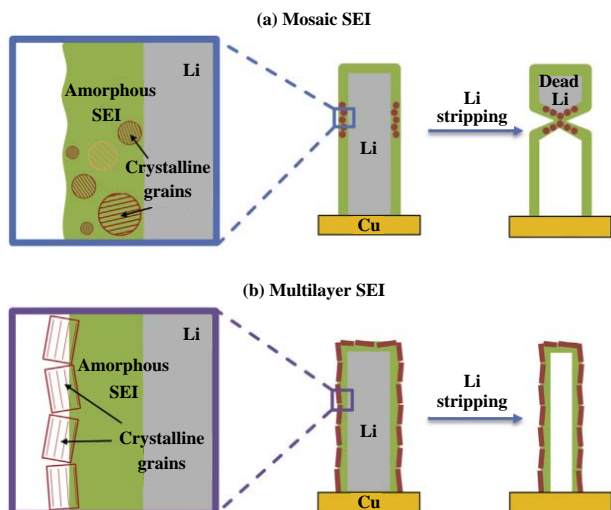
Figure 10 Mosaic and multilayer SEI nanostructure. (a) Schematic of the mosaic SEI nanostructure forms on lithium metal in EC/DEC electrolyte. Crystalline grains are heterogeneously dispersed within a polymeric and amorphous matrix. (b) Schematic of the multilayer SEI nanostructure that forms on lithium metal in 10 vol.% FEC electrolyte. Reproduced with permission from Ref. [111], © Elsevier Inc. 2018.

Figure 11 Schematic figures of the initial SEI generated on graphite anodes for electrolytes. Reproduced with permission from Ref. [114], © Elsevier Inc. 2019.

distributed in the amorphous matrix covering the lithium metal. The matrix may be an organic polymer formed by the decomposition of a carbonate electrolyte. The SEI formed in this electrolyte is similar to the mosaic structure predicted by Peled [5]. When 10 vol.% FEC is added to the electrolyte, a different SEI structure is observed. The SEI formed in the presence of FEC is more ordered and appears to have a multilayer structure, which is consistent with the multilayer system proposed by Aurbach [28]. As mentioned in Section 2, the mosaic structure is more likely to form lithium dendrite and "dead Li". The layered structure reduces the generation of "dead Li" and avoids local preferential stripping of Li.

4 Electrolytes

The electrolyte mainly consists of lithium salt, organic solvents, additives, and trace amounts of impurities. The organic solvents or additive undergoes a reduction reaction on the anode surface during the first charging process, forming the SEI film. Due to the different decomposition potentials of the solvents or additives, the thickness and composition of the SEI film are also different. For instance, some film-forming additives will form a film before the solvents decompose, inhibiting the decomposition of the solvents. Due to the difference in additives, the thickness, stability, and resistance of the SEI film will also be changed [113]. Besides, impurities such as alcohol, water, and hydrofluoric acid (HF) acids are unavoidably present in the raw material of the electrolyte. When the methanol content exceeds a particular value, it will react at around 2.0 V to form lithium methoxide, resulting in a sparse and thin SEI film [112].

The composition of SEI film is also related to the ingredient of the electrolyte. Figures 11(a) and 11(b) summarize the differences in the structure of SEI [114]. The preferential reduction of vinylene carbonate (VC) leads to a decrease in the concentration of lithium ethylene dicarbonate (LEDC) and an increase in the concentration of Li_2CO_3 in the anode SEI. Besides, poly-VC also exists in SEI and has an apparent cross-linking effect, which improves the stability of SEI. The preferential reduction of FEC also leads to a decrease in the concentration of LEDC and an increase in the concentration of Li_2CO_3 in SEI. A higher concentration of LiF is also observed during the reduction from FEC to LiF, resulting in the formation of poly-VC. The difference
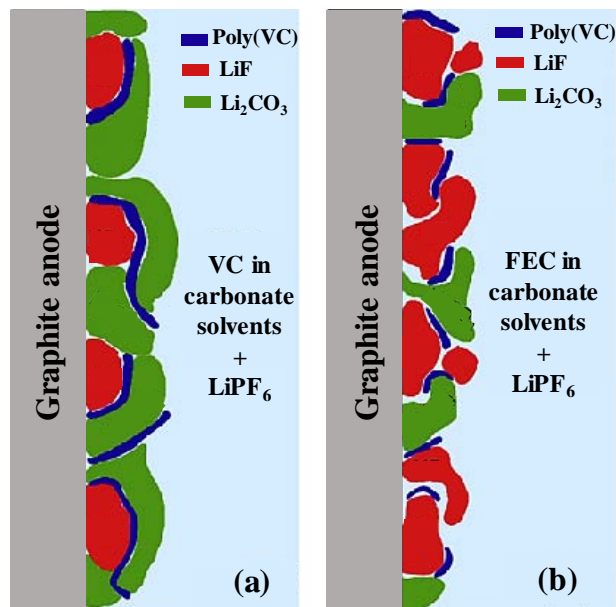
in the reduction reaction and product led to the performance difference between VC and fluoroethylene carbonate (FEC). Qin et al. recently proposed an *in situ* cross-linking strategy for stabilizing the LEDC of the solid-electrolyte interphase in lithium ion batteries, and this provides a new avenue and insight into the design of SEI film on anode materials [115]. Now we will discuss the influence of electrolytes on SEI film in detail from three aspects: electrolyte salts, solvents, and electrolyte additives.

4.1 Electrolyte salts

It is generally considered that the supporting electrolyte salt as the solute is more easily reduced than the solvents and the reduced product becomes part of the SEI film [94]. However, there are always various defects in commonly used electrolytes. For instance, $LiClO_4$ is a strong oxidant that has poor safety. $LiAsF_6$ has the best electrochemical performance on the anode electrode but is highly toxic. $LiPF_6$ is one of the most popular lithium salts in commercial batteries. Due to the low association of PF_6^-, the electrolyte with $LiPF_6$ as the lithium salt has high conductivity (1 M $LiPF_6$-EC + DMC electrolyte has a conductivity of 10^{-2} S/cm at room temperature). $LiPF_6$ decomposes on the surface of the lithium electrode to form LiF, which can stabilize the interface of the lithium electrode. However, only a tiny amount of $LiPF_6$ decomposes into LiF at 60 to 80 °C. Therefore, searching for new lithium salts has been continuously carried out. The property comparison of several commonly used lithium salts is exhibited in Fig. 12 [116, 117].

The main difference between electrolyte lithium salts is the type of anions that will affect the formation of the potential and chemical composition of the SEI film. The decomposition of inorganic lithium salts may also directly generate these compounds: $LiPF_6$ (solve) → LiF (s) + PF_5 (s). Due to the propensity to thermodynamically produce inorganic lithium compounds, the SEI film can be more stable. The presence of compounds weakens the dissolution and destruction of the SEI film during electrochemical cycling. As for lithium salt, the solvent molecules and the lithium salt anions decompose at different potentials during the lithium electrode cycle. The polymer passivation layer leads to a significant increase in the resistance of the SEI film. In the discharge process, lithium ions mainly formed a lithium ion-conducting passivation layer with an inorganic salt. The above-described process results in non-uniformity of the
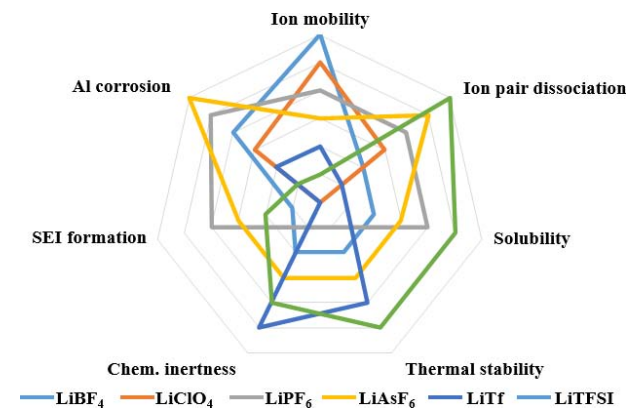
Figure 12 Comparison between salts for lithium batteries.

ionic conductivity, resistance, and thickness of the SEI film, leading to a low cycle efficiency. Anions are not solvated in the electrolyte, but Peled [116] believed that the reaction rate of anions with solvated electrons is an essential factor in determining the formation potential of the SEI film.

In recent studies, Kondou et al. have demonstrated significant improvement in the cycle performance of a $Li_4Ti_5O_{12}$ electrode using a Li-Ca binary salt hydrate (LCH) electrolyte in combination with an optimized electrochemical pretreatment process. This is because the LCH electrolyte provides less water-soluble calcium-based SEI components and can form a thicker SEI layer on the $Li_4Ti_5O_{12}$ electrode, effectively reducing the adverse side reactions. This provides a promising way to stabilize the formation of the SEI layer for the practical use of low potential anode materials in waterborne rechargeable lithium-ion batteries [118]. In the work of Liu et al., excellent cycling stability of lithium metal anodes was achieved by utilizing a novel dual-salt electrolyte based on lithium bis(fluorosulfonyl) imide (LiFSI) and lithium difluorobis (oxalato) phosphate (LiDFBOP) in carbonate solvents. The preferential reduction of LiDFBOP occurs prior to LiFSI and carbonate solvents and its reduction products ($Li_2C_2O_4$ and P-O species) bind to LiF, resulting in a favorable compact and protective SEI on the Li electrodes. This work demonstrates that constructing a tailored SEI using a dual-salt electrolyte system is vital for improving the interfacial stability of lithium metal batteries [119]. Through *ab initio* molecular dynamics simulations, Kuai et al. found that lithiation and electron transfer are the triggering factors for $LiPF_6$ degradation, and higher electrolyte dielectric constant and lithiation extent profoundly assist the $LiPF_6$ decomposition. These findings promote rational SEI engineering and electrolyte tuning for enhancing the performance of lithium metal anodes [120].

4.2 Solvents

Solvent molecules and lithium salts are decomposed and deposited at different speeds under different electrochemical potentials. The non-uniform deposition of the reaction product on the surface of the electrode results in the SEI film with non-uniform electronic conductivity and lithium ion conductivity. This causes the difference in the film thickness and reactivity during subsequent cycles. Yang studied the composition of SEI film in various solvents [121, 122]. For instance, in the propylene carbonate (PC) solution, the formed SEI film cannot completely cover the surface of anodes, which leads to an easy reaction between the electrode surface and electrolyte, generating irreversible capacity. When pure EC is used as the solvent, the main component of the formed SEI film is $(CH_2OCOOLi)_2$. Differently, when adding DEC or DMC in EC solvent, the main components of the formed SEI film are C_2H_5COOLi and Li_2CO_3. The latter two formed a more stable SEI film than that of pure EC. Additionally, in EC/DEC and

EC/DMC hybrid systems, EC is the primary source of SEI film formation. The prominent role of DEC and DMC is to increase the conductivity and solubility of the solution rather than participating in the formation of SEI film. Besides, the CO_2 produced by the decomposition of esters promotes a stable SEI film. Peled et al. analyzed the lithium intercalation performance of SEI film under high temperature conditions using several ratios of EC/PC and EC/DMC as solvents. Studies have shown that PC containing electrolyte at room temperature will form a non-uniform passivation layer on the surface of the electrode, which is easy to cause solvent co-embedding to destroy the electrode. Moreover, the addition of PC is beneficial to improve the high-temperature cycle performance and reduce the irreversible capacity of the electrode. Further research about the mechanism is needed.

4.3 Electrolyte additives

The strategy of adding electrolyte additives to the electrolyte is a more straightforward method to enhance the strength of SEI layer, which can efficiently control the growth of lithium dendrites. Some typical additives have been widely explored and indeed taken effect on lithium dendrite suppression, such as hydrofluoric acid [37], FEC [123], vinylene carbonate [124], trace-amount of water [125], $CsPF_6$ [126], thionyl chloride [127], and tris (2,2,2-trifluoromethyl) borate [128], $LiNO_3$ [129], LiF [130], phosphates [131], thiourea (THU) [132], crown ethers (the 15-crown-5 (15-C-5)) [133], boron nitride [134], and 1-octyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([OMIm]TFSI) [135]. The content of additives in the electrolyte does not exceed 5% by weight or volume, but its presence significantly improves the cycle performance of lithium batteries [14]. The additives can promote the formation of SEI on the electrode surface and reduce the adverse effects of SEI generation, such as irreversible capacity and gas generation. According to the different ways in which additives act, they are divided into reducing additives and reactive additives.

For reduction type additives, such additives generally have a higher reduction potential than the electrolyte solvents. Before the electrochemical reduction of the electrolyte solvents, the additives are reduced to insoluble solid products, which cover the electrode surface to passivate the catalytic activity. Therefore, the use of these additives not only minimizes the generation of gas but also improves the stability of SEI due to the partial participation of additive molecules in SEI [136].

VC is a kind of organic film additive with the most in-depth research and ideal effect [137]. Its reduction potential is higher than those of EC, PC, DEC, DMC, and other organic solvents. In the anode, VC is preferentially reduced and a polymerization reaction occurs. The polymer helps increase the elasticity of the SEI film, thereby optimizing the interface properties of the electrode. The addition of 2 wt.% VC to 1 M $LiPF_6$-EC + DMC can significantly increase the Coulombic efficiency of the electrode at room temperature and high temperature while reducing the evolution of gases (C_2H_4 and CH_4) due to the decomposition of EC and DMC [138]. Adding 5 wt.% VC to 1 M $LiClO_4$-PC can also make lithium deposition more uniform and improve the Coulombic efficiency of lithium electrodes [139]. Besides, similar additives include vinyl ethylene carbonate [140], allyl ethyl carbonate [141], vinyl acetate [142], divinyl adipate [143], acrylic acid nitrile [144], 2-vinyl pyridine [145], and maleic anhydride [146].

Reducing agents assist the formation of SEI by adsorbing their reduction products to the active catalytic center. Furthermore, most of these additives are sulfur-based compounds, including SO_2 [147], CS_2 [148], polysulfide (S_x^{2-}) [149], cyclic alkyl sulfites such as ethylene sulfite [150], propylene sulfite [151], and aryl

sulfites [152]. The existence of sulfide can accelerate the diffusion rate of lithium ions through SEI layers. However, too much sulfur in the SEI will also cause the instability of the anode, especially under the condition of high potential [153].

Moreover, other reductant additives include N_2O [154], nitrates [155], halogenated ethylene carbonate [156], and FEC [157]. As the most commonly used electrolyte additive, FEC can create polymeric or oligomeric species due to the polymerization of VC, resulting from the FEC decomposition (Fig. 13). Thus, FEC can effectively improve the cyclic performance of metallic lithium anodes [14].

As for reaction type additives, they may not be electrochemically reduced in the entire potential range of lithium ions insertion. But, they can scavenge the free radical anions of intermediate compounds, which are reduced by the solvents, or combine with the final products such as lithium alkyl carbonate and lithium alkoxy to form a more stable SEI [14]. Early reports on this type of additive are that the presence of CO_2 reduces the initial irreversible capacity and stabilizes the SEI [158]. For instance, Osaka significantly improved the cycle efficiency of the lithium electrode by 1 M $LiClO_4$-PC electrolyte dissolved in CO_2 [159, 160]. Besides, Gan introduced CO_2 into electrolyte 1 M $LiAs_6$-PC: DME (1:1 vol.%). The results show that the lithium electrode interface impedance is significantly reduced [161]. This performance improvement should be attributed to the existence of Li_2CO_3, which possesses low electrical resistance, and can highly reduce the side reaction of the electrolyte and the electrode [160]. This tight layer also has excellent protection for the electrode. Therefore, two reactions can be proposed to explain that CO_2 promotes the formation of SEI (Fig. 14 below) [14].

Beyond that, carboxy phenols [162], aromatic esters [162], and acid anhydrides [163] can improve the formation of SEI. These compounds have an excellent conjugated structure, which can stabilize intermediates through the delocalization of free radicals. Other additives with similar functions include maleic anhydride [146], succinimide, and N-benzyloxy carbonyloxy succinimide [164], in which two radical anions delocalize the "N" atom. The carbonyl group is attached. These additives are very effective in inhibiting stable SEI. The additive does not involve reduction and forms more stable radical anions by trapping less stable solvent radical anions.

In other cases, the solvent molecules and the lithium salt anions are almost all decomposed in the same potential region during the cycling of the lithium electrode, which means that during the charge and discharge cycle of the lithium electrode, the solvent
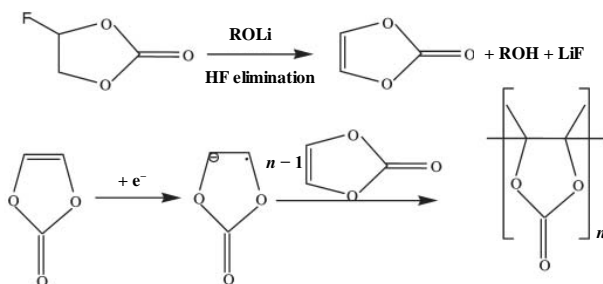

Figure 13 Reduction mechanism of FEC, which leads to the formation of polymeric species.
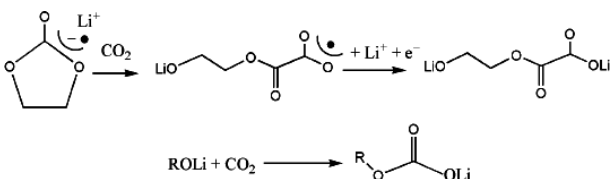

Figure 14 The mechanism of the CO_2 stabilizes the SEI. Reproduced with permission from Ref. [14], © Elsevier B.V. 2006.

molecules and the lithium salt anions are decomposed. Simultaneously, the SEI film with relatively uniform ionic conductivity, resistance, and thickness is formed on the surface of the lithium electrode, and the Coulombic efficiency of the lithium anode is relatively high.

Therefore, to form a uniform SEI film, the electrolyte should have the following characteristics: (1) Solvent molecules and lithium salt anions should have similar decomposition rates; (2) During the cycling of the lithium electrode, solvent molecules and lithium salt anions should decompose under similar potentials; (3) Electrolyte additives can decompose before electrolyte, and the decomposition products should possess good mechanical or electrochemical properties, promoting the formation of SEI and reducing the by-products produced during the cycles.

5 Conclusions, challenges, and perspectives

In conclusion, this review discusses the basic science and the latest progress of SEI in lithium batteries. Strategies to obtain stable SEI based on the analysis of discrepancies in SEI formation on different types of anode materials, and the function and effects of electroactive materials are summarized and discussed. The interaction between artificial SEI and anode still needs to be studied in depth to guide the design of structure and function. We believe that a deeper understanding of the scientific fundamentals can help address challenges arising from the side reaction at the electrolyte–electrode interface, and the mentioned solutions can assist in designing stable and efficient SEI for developing high-energy-density lithium batteries.

Although achievements have been made in the field of SEI, enormous challenges still need to be overcome in future research: 1) The formation mechanism, composition, structure, lithium ion diffusion pathway, and dynamic evolution behavior of SEI are not fully understood; 2) The influence of different chemical components in SEI on dendrite growth has not been systematically studied; 3) The thickness, density, and lithium ion conductivity of artificial SEI cannot be flexibly manipulated. A simple and low-cost method to achieve large-scale production of artificial SEI in the future is a prerequisite for its practical application; 4) From the perspective of commercial development, SEI stability needs to be analyzed under more stringent conditions (dilute electrolyte, thin lithium foil, high current density, and capacity). In order to improve the SEI of lithium batteries, many electrolyte additives can be used. However, in many cases, the use of additives will more or less improve the target performance while introducing other negative effects. For example, an appropriate amount of VC is conducive to SEI and lithium cycle formation, but excessive VC will lead to low cell cycle efficiency and a high self-discharge rate. The results of mixed salt solutions are also quite impressive, such as $LiFAP/LiPF_6$, $LiBOB/LiPF_6$, and $LiBF_4/LiODFB$. Thus, further research is need to understand the mechanism.

The development of nanotechnology, physics, chemistry, electrochemistry, materials science, and advanced characterization technology has made it possible to solve these problems through interdisciplinary research. Therefore, with the continuous development of science and technology, nano-metal protection will become a powerful research field. We believe that this timely review will promote a further understanding of SEI and explore stable and robust SEI technology. A sense of SEI-related phenomena is essential for developing safer and better lithium batteries. According to recent research, we have a good knowledge of the SEI formation process, the dynamics of the SEI electrode, and the growth of the SEI in typical systems, mainly lithium ions and lithium metal batteries. However, in general, the actual SEI

does not seem to have optimal properties, as they grow continuously in repeated cycles of charge and discharge and are stored and dissolved at high temperatures for long periods, leading to dangerous conditions. However, SEI will also improve battery performance if SEI is actively applied, which is worthy of further discussion in future research.

The formation process of SEI film is complex and influenced by many factors, making it difficult to conduct systematic research. Nonetheless, SEI film is an indispensable component of lithium batteries. Based on existing research, future directions of SEI research may focus on the following aspects:

(1) Modification of anode materials for more stable SEI. Continuous exploration of modification methods for different types of anode materials, such as coatings with more flexibility and higher mechanical strength, or structural optimization are used to obtain a more stable SEI film.

(2) Modification of electrolytes for more efficient SEI. In order to meet the needs of current practical applications, it is urgent to optimize liquid formulations and search for new solvents, lithium salts, or additives with excellent properties. In this process, exploring the mechanism and function of SEI film formation of various new-type electrolyte components will point out the direction of the development of electrolyte formulations.

(3) Designing new types of artificial SEI film for directional control of morphology and structure. At present, in addition to the research on the performance of artificial SEI film, it is more important to analyze the research process of improving the electrochemical performance of battery through artificial SEI film in detail. Therefore, in future research work on artificial SEI film, more attention should be paid to the research of SEI structure and formation mechanism.

(4) Advanced characterization technology. Traditional *ex situ* characterization methods make it difficult to systematically research and analyze SEI films. Thus, it is important to develop effective *in situ* analysis methods that can accurately and dynamically detect changes in SEI films under the working conditions of lithium batteries. Therefore, further research should focus on developing advanced techniques such as improved cryoelectron microscopy and nuclear magnetic resonance. In addition, since different characterization methods provide different perspectives on SEI film research, more targeted characterization methods should be adopted for key research issues in future research.

(5) Strengthening theoretical calculation to provide guidance for the experiments. Theoretical calculations of material surface state and reaction activity can provide important guidance for studying SEI films. In addition to the optimization and innovation of the simulation calculation model, the actual objective analysis and experimental conclusion support of the structure and mechanism of SEI film should also be strengthened. Moreover, future research should focus on establishing the relationship between SEI phase structure and performance. In a word, future research should prioritize investigating SEI mechanisms and strengthening fundamental theory research.

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