

Mini Review

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Ionic conductivity and mechanical properties of the solid electrolyte interphase in lithium metal batteries

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Abstract

With the fullness of time, metallic lithium (Li) as an anode could become highly promising for high-energy-density batteries. Theoretically, using Li metal as the negative electrode can result in higher theoretical capacity and lower oxidation voltage and density than in current commercially available batteries. During the charge/discharge process, however, metallic Li shows unavoidable drawbacks, such as dendritic growth, causing capacity degradation and a solid electrolyte interphase (SEI) layer derived from the side reactions between the Li metal anode and the electrolyte, resulting in depletion of the electrolyte. The formation of a suitable SEI is crucial to avoid the side reactions at the interface by circumventing direct contact. Unavoidable dendritic growth at the Li metal anode can be controlled by its ionic conductivity. Furthermore, the SEI is also required as a mechanical reinforcement for withstanding the volume change and suppressing dendritic growth in the Li metal anode. A limiting factor due to complex SEI formation must be considered from the perspectives of chemical and mechanical properties. To further enhance the cycling performance of Li metal batteries, an in-depth understanding of the SEI needs to be achieved to clarify these issues. In this mini review, we focus on the SEI, which consists of various deposited components, and discuss its ionic conductivity and mechanical strength for applications in electric vehicles.



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Keywords: Electrolyte additive, ionic conductivity, lithium dendrite, lithium metal battery, solid electrolyte interphase (SEI), solid electrolyte

INTRODUCTION

Lithium (Li)-ion batteries play an important role in applications for extending the operating hours of small information technology devices and the driving mileages of electric vehicles^[1-3]. In particular, although high-energy-density batteries are desirable, commercial lithium-ion batteries based on a graphite anode cannot provide sufficient energy density. Even if a newly developed structure or material is applied in the electrodes, it is not easy to achieve a gravimetric energy density as high as 300 Wh kg⁻¹. One method to overcome this challenge is to replace the existing graphite or silicon additive anode^[4]. Li metal is an ideal anode material for achieving high energy density, owing to its high theoretical capacity (3860 mAh g⁻¹), low redox potential (-3.04 V vs. a standard hydrogen electrode) and low density (0.534 g cm⁻³)^[5]. Moreover, it is known that the performance of Li metal batteries can be further enhanced by adapting high-voltage lithium nickel cobalt manganese oxide cathodes^[6]. During Li plating and stripping, however, inherent dendritic growth, uneven solid electrolyte interphase (SEI) formation and Li volume expansion are unavoidable issues that trigger internal short-circuiting in Li metal batteries^[7].

The electrolyte has a profound impact on the electrochemical cycling of the Li metal anode. On the surface of Li metal, an SEI layer is formed by accumulating various decomposition products created by a chemical reaction with the organic electrolyte^[8-10]. This SEI layer provides passivation to prevent Li metal corrosion by preventing contact between the electrolyte and the Li metal^[11]. However, it is difficult to predict the electrical properties of SEI layers because their heterogeneous phases vary depending on the type of organic electrolyte^[12-14]. The primary issue is that Li electrodeposition is locally concentrated along any cracks in the SEI layer, leading to various side reactions inside the electrode^[15,16]. During repeated plating and stripping, particles of inactive dead Li are gradually accumulated, resulting in performance degradation. Given these difficulties, the utilization of metallic Li anodes still faces many challenges for commercial viability, especially dendritic Li growth^[17].

So far, various approaches have been developed to suppress dendritic Li growth. For example, electrolyte additives have been used to achieve high ionic conductivity, separator design has been proposed to improve dendritic blockage, interlayer coatings have been utilized to stabilize the Li metal surface and host architectures that can store Li metal have been developed. Li is a highly active material that reacts with all organic electrolytes, leading to SEI layer formation^[18-23]. In particular, the thickness of the SEI layer shows unlimited growth until both the organic electrolyte and the metallic Li are entirely consumed. SEI growth mechanisms are difficult to understand due to the variety of organic electrolytes utilized^[24]. We know that the high ionic conductivity (σ_{SEI}) of an SEI effectively suppresses the dendritic Li growth during Li plating and stripping. Nevertheless, there remains doubt regarding which component entirely governs the σ_{SEI} ^[22]. In this mini review, we summarize the σ_{SEI} of each SEI phase and provide insights to understand and predict the phenomenon of dendritic Li growth.

Solid electrolyte interphase

The SEI model was first suggested by Dey and further developed by Peled^[25,26]. The SEI as a passivation layer is known to be a unique feature with simultaneous ionic conductivity and insulating properties. It consists of different heterogeneous components, such as semi-carbonates, polyolefins, lithium oxide (Li₂O), lithium carbonate (Li₂CO₃) and lithium fluoride (LiF), as shown in [Figure 1](#)^[12,27]. Significant effort has been devoted

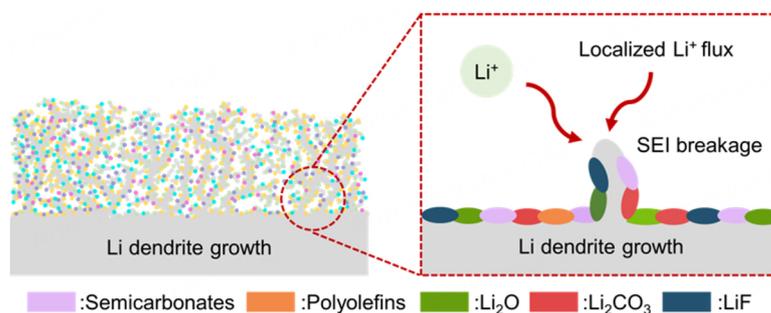


Figure 1. Schematic illustration of a Li dendrite with various SEI components. Owing to the cracks generated during the charge/discharge process, Li metal is exposed to the electrolyte and a localized Li-ion flux occurs.

to further understanding the formation of the heterogeneous components. Spotte-Smith and co-workers reported the formation mechanism of the key components of the SEI and gaseous byproducts through computational reaction networks containing over million reactions and kinetic Monte Carlo simulations^[28].

Interestingly, the mechanisms of the formation of SEI components are affected by the potential of the Li metal anode. Sun and co-workers verified that a bilayer SEI was formed when the potential of the Li metal anode was below 0.1 V (*vs.* Li/Li⁺)^[29]. The inner layer was composed of more inorganic compounds, such as Li₂O, lithium nitride (Li₃N), LiF, lithium hydroxide (LiOH) and Li₂CO₃ (4.4% for SEI of Li metal anode at 0 V), whereas the outer layer was composed of more organic compounds, such as ROCO₂Li, ROLi and RCOO₂Li (16.8% for SEI of Li metal anode at 0 V). Furthermore, when the potential of the Li metal anode was below 0 V (*vs.* Li/Li⁺), inorganic components were primarily generated on the Li metal anode^[29]. Ideally, the SEI requires high Li-ion conductivity, low electronic conductivity and high thermal and mechanical stability for fast Li-ion kinetics, reduced electrolyte depletion and minimal volume expansion. As the thickness of the SEI layer gradually increases during Li plating and stripping, its weak mechanical properties are insufficient to accommodate the significant volume expansion of up to 300%^[10,30,31]. If tiny cracks, known as “hot spots”, exist on the SEI layer, they are directly exposed to the organic electrolytes, such as carbonate and ether bases^[15,16]. The uneven Li-ion flux then has a tendency towards local penetration and subsequently accumulates at these spots, leading to inactive or dead Li and then to capacity and cyclability losses. In addition to dead Li, dendritic Li growth is an unavoidable feature, which must be suppressed, because the introduction of dendritic growth consumes both the Li anode and the electrolyte until cell failure^[32].

In addition, the ionic conductivity of the SEI (σ_{SEI}) determines the morphology of the Li metal anode by affecting the pathways of Li ions in the SEI layer, owing to the potential field caused by its low conductivity^[33]. Ma and co-workers reported the Li-ion transport mechanism in inorganic SEI components such as LiF, Li₃N, Li₂O, LiOH and Li₂CO₃. Interestingly, the bulk ionic conductivity of inorganic SEI components is extremely low. However, relatively high ionic conductivities were found at the interface of different types of inorganic SEI components. In particular, at the interface between LiF and Li₂O, the ionic conductivity ($1.96 \times 10^{-4} \text{ S cm}^{-1}$) is extremely improved compared to the bulk materials (5.2×10^{-10} and $10^{-9} \text{ S cm}^{-1}$, respectively). This indicates that the Li ions migrate through grain boundaries to increase the ionic conductivity of the SEI^[34-36].

Figure 2A shows the process of Li deposition with a conventional electrolyte-deposited SEI with poor ionic conductivity ($< 10^{-6} \text{ S cm}^{-1}$). Initially, the SEI layer is formed owing to an unintended and unavoidable side reaction between the electrolyte and the Li metal anode. Due to the formation of the SEI layer with low ionic conductivity, Li ions intensively penetrate specific areas. Once Li ions are deposited on the Li metal

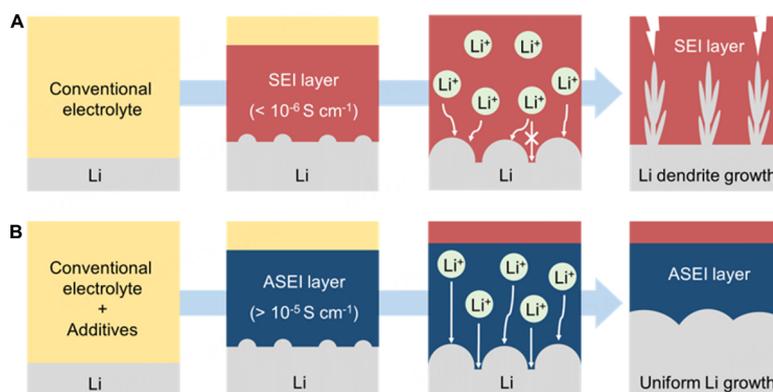


Figure 2. Schematic illustration of Li metal dendrite growth process in conventional electrolyte (A) without and (B) with additives.

electrode, they form branch-shaped structures known as dendrites, more localized and non-uniform Li-ion flux occurs, and as a result, dendrite formation is accelerated. To avoid dendrite growth by localized Li-ion flux, intensive research has been undertaken to introduce additives into the electrolyte to improve the ionic conductivity. **Figure 2B** shows the process of Li deposition with an artificial SEI, which has a high ionic conductivity ($> 10^{-5}$ S cm⁻¹). The localized Li-ion flux caused by the low ionic conductivity of the SEI layer is diminished, and as a result, the Li metal grows uniformly, because Li ions are evenly deposited in all areas^[37-42].

Ionic conductivity measurements

Uneven Li deposition is well known to occur due to the heterogeneous ionic conductivity of the native SEI on a Li metal surface. The ionic conductivity (σ_{SEI}) can be calculated by alternating current impedance spectroscopy^[27,43]. Experimentally, in this method, a sinusoidal potential is applied over a wide frequency range to an electrochemical cell with blocking electrodes as ideal capacitors and its response is recorded. As shown in **Figure 3**, a typical equivalent circuit for Li metal with an SEI can be classified into six components: (i) bulk resistance of the cell (R_{Bulk}); (ii) SEI resistance of the interfacial layer (R_{SEI}); (iii) charge transfer resistance (R_{CT}); (iv) capacitance of the interfacial layer (CPE_{SEI}); (v) double-layer capacitance ($\text{CPE}_{\text{Electrode}}$); and (vi) Warburg component, reflecting the diffusional effects of Li on the host materials. The ionic conductivity (σ_{SEI}) is calculated by

$$\sigma_{\text{SEI}} = \frac{1}{\rho_{\text{SEI}}} = \frac{1}{R_{\text{SEI}}} \cdot \frac{d}{A_{\text{act}}}, \quad (1)$$

where ρ_{SEI} is the specific ionic resistivity, R_{SEI} is the specific ionic resistance, d is the thickness and A_{act} is the active cross-sectional area. It should be noted that ρ_{SEI} and R_{SEI} are the only material properties that are independent of geometry. Han and co-workers calculated the ionic conductivity of a lithium-rich antiperovskites (LiRAP) film (10^{-4} S cm⁻¹), which was considered as an artificial SEI. A LiRAP-ASEI with a thickness of 1 μm on copper (Cu, 1.6 cm in diameter) disks was used for EIS measurements and R_{SEI} was estimated to be 13 Ω ^[44]. Such values are not easy to evaluate from direct experiments^[45,46] and many researchers have therefore suggested alternative approaches, i.e., theoretical calculations.

Notably, the σ_{SEI} is governed by the accumulated components of the SEI. The σ_{SEI} is estimated to vary from 10^{-4} to 10^{-12} S cm⁻¹^[47-49]. A relatively low value is known to cause dendritic Li growth in Li metal anodes. Among the components, LiF, Li₂CO₃, Li₂O and Li₃N are representative and correspond to ionic

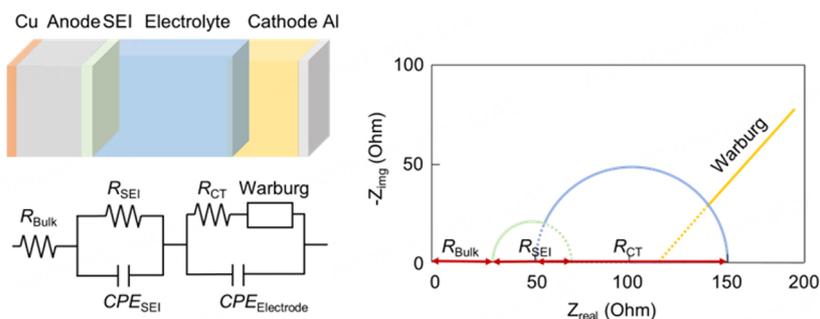


Figure 3. Schematic illustration of battery components, equivalent circuit model and Nyquist plot of the internal resistance of a Li-ion battery. The diameters of the green and blue circles indicate R_{SEI} and R_{CT} , respectively. The yellow line indicates the Warburg impedance in the low-frequency region.

conductivities of 6.0×10^{-6} - 5.2×10^{-10} , 6.7×10^{-8} , 10^{-9} - 10^{-12} and 1.2×10^{-4} S cm^{-1} , respectively. The nature of the SEI can provide clues to achieving insights into dendritic Li growth. Table 1 summarizes the experimental and theoretical values of the Li-ion conductivity of the SEI layer derived from various additives. The organic phases of the SEI can accommodate part of the electrolyte, thereby enhancing the Li-ion conductivity.

STRATEGIES FOR MINIMIZING DENDRITIC LITHIUM GROWTH

Electrolyte additives

During Li plating and stripping, an organic electrolyte is decomposed into Li_2O , Li_2CO_3 , LiF, LiOH and so on. These components have poor Li-ion conductivity at the interface with Li metal. These components affect cell performance due to their low ionic conductivity. Instead of the natural SEI, a new strategic, artificial SEI with high ionic conductivity is required to suppress dendritic Li growth. In addition, it is also capable of inhibiting dendritic Li growth with high mechanical strength^[12].

Interestingly, high ionic conductivity at the Li metal interface decreases the overpotential during Li plating and stripping, thereby stabilizing the SEI. For this purpose, stable SEI components, such as Li_3N , lithium sulfide (Li_2S), lithium aluminate (LiAl_5O_8), lithium phosphide (Li_3P) and ternary lithium aluminum fluoride (Li_3AlF_6), have been developed using various combinations of Li additives. In particular, Li salts, including lithium nitrate (LiNO_3) and Li_xS_y , are widely used to improve the interfacial stability of Li metal anodes in ether-based electrolytes^[67]. In detail, LiNO_3 decomposes into Li_3N and Li_2O , and Li_3N is the key component due to its high ionic conductivity (1.2×10^{-4} S cm^{-1}) for this purpose. Lithium bis(fluorosulfonyl)imide (LiFSI)- LiNO_3 in a dimethyl ether electrolyte was found to minimize the dendritic Li growth. This is strongly related to the high ionic conductivity of the LiF- and Li_3N -rich SEI layers. Moon and co-workers reported a correlation between SEI thickness and ionic conductivity, as shown in Figure 4A. Regardless of the thickness of the SEI, the Li_3N -rich SEI layer introduced a small potential change, resulting in uniform Li growth^[37]. In addition, a thicker Li_3N SEI layer causes higher ionic conductivity, although the LiNO_3 additive has the feature of low solubility in carbonate-based electrolytes^[68]. Moreover, carbonate-based electrolytes have stronger reactivity than ether-based ones toward Li metal.

Recently, significant efforts to use LiNO_3 additives in carbonate-based electrolytes have been made to enable the adoption of high-voltage batteries. Even if LiNO_3 is incompletely dissolved in a carbonate-based electrolyte, the highly concentrated LiNO_3 additive in ethylene carbonate and diethyl carbonate yielded a stable SEI and outstanding cell performance during Li plating and stripping. Figure 4B summarizes the solubility of the LiNO_3 additive in different carbonate-based electrolytes^[69]. The maximum concentration of NO_3^- was investigated in different carbonate-based electrolytes through colorimetry by cadmium reduction

Table 1. Ionic conductivity of natural SEI and artificial SEI components

| SEI components | Ionic conductivity ($S\text{ cm}^{-1}$) | Ref. |
|------------------------------------------------------|----------------------------------------------|---------|
| LiF | 6.0×10^{-6} - 5.2×10^{-10} | [50,51] |
| LiF-Li ₂ CO ₃ | 3.0×10^{-6} - 3.0×10^{-7} | [52] |
| Li ₂ O | 10^{-9} - 10^{-12} | [50,53] |
| Li ₂ CO ₃ | 6.7×10^{-8} | [52] |
| Li ₂ EDC | 4.5×10^{-9} | [54] |
| Li ₃ N | 1.2×10^{-4} | [55] |
| PEO _m -5%Li ₂₁ Si ₅ | 3.9×10^{-5} | [56] |
| LiZrO(NO ₃) ₂ | 2.3×10^{-6} | [57] |
| LiAl ₅ O ₈ | 3.2×10^{-6} | [58] |
| SPVA | 1.59×10^{-6} | [59] |
| Li ₃ P | 10^{-4} | [60] |
| LiRAP film | 10^{-4} | [44] |
| LiF/Li ₃ Sb-5 layer | 1.01×10^{-5} | [61] |
| [LiNBH] _n | 6.6×10^{-6} | [62] |
| Li ₂ S | 10^{-5} | [63] |
| Li ₃ AlF ₆ | 10^{-5} | [64] |
| FE-Li/Na | 1.1×10^{-5} | [65] |
| FE-Li | 4.57×10^{-6} | [65] |
| LIPON | 1.1×10^{-6} - 1.4×10^{-6} | [46,66] |

Li₂EDC: Dillithium ethylene decarbonate; PEO: poly(ethylene oxide); SPVA: sulfonated poly(vinyl alcohol); LiRAP: lithium-rich anti-perovskite; FE: fluorinated etching; LIPON: lithium phosphorus oxynitride.

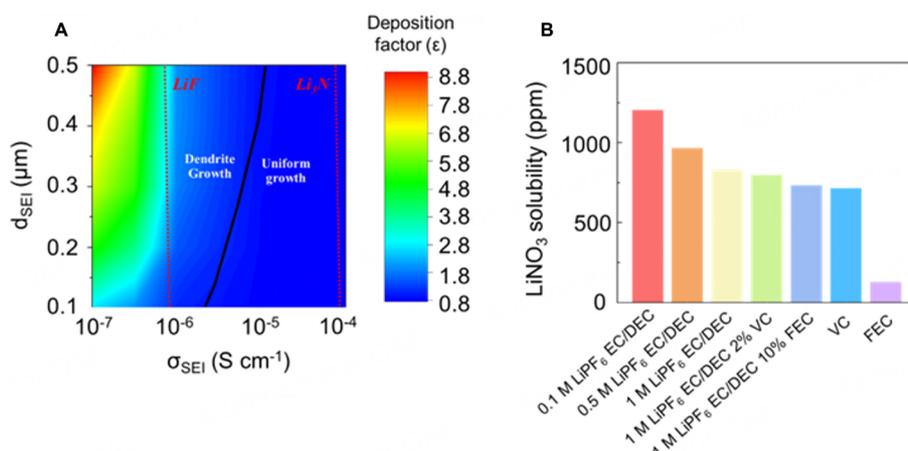


Figure 4. (A) Contour plot of deposition factor as a function of ionic conductivity and thickness of SEI layer. Reproduced from Ref. [37] with permission from the Royal Society of Chemistry. (B) Solubility of LiNO₃ in different carbonate-based electrolytes. Reproduced from Ref. [69] with permission from Nature.

using a discrete analyzer. The solubility of the LiNO₃ additive in carbonate-based electrolyte is one order of magnitude smaller than that in an ether-based one. On decreasing the concentration of LiPF₆, the solubility of NO₃⁻ noticeably increases, which is known as the “common-ion effect”. Brown and co-workers found that using phosphate solvents increases the solubility of additives in carbonate-based electrolytes. Specifically, triethyl phosphate significantly increases the solubility of LiNO₃, resulting in an improvement in the capacity retention and Coulombic efficiency^[70].

In addition to LiNO_3 , Li_xS_y is a potential additive candidate that forms Li_2S and Li_2S_2 . The ionic conductivity of bulk Li_2S is extremely low ($\sim 10^{-26} \text{ S cm}^{-1}$). However, when Li_2S exists as a thin layer at the interface, owing to the grain boundaries, dislocations, interfaces and amorphous content, its ionic conductivity ($10^{-5} \text{ S cm}^{-1}$) is higher than other common SEI components, such as Li_2CO_3 ($10^{-8} \text{ S cm}^{-1}$) and LiF ($3 \times 10^{-9} \text{ S cm}^{-1}$)^[71-73]. The Li_xS_y additive also results in a mechanically dense and thick SEI layer on the surface of Li metal, because Li metal reacts with Li_xS_y to form an insoluble component^[74]. Note that the passivation layer derived from the LiNO_3 additive is less solid. Some synergistic effects can be expected from using dual LiNO_3 - Li_xS_y . This approach causes flat Li plating without dendritic Li growth in ether-based electrolytes. This feature cannot be achieved using only LiNO_3 ^[75]. In a similar manner, dendritic Li growth can be inhibited by using a dual-layer composed of an organic layer and an inorganic layer. Zhang and co-workers reported a uniform and compact dual-layer SEI with organic components (e.g., ROLi and ROCO_2Li) on the top layer and inorganic components (e.g., LiF and Li_2CO_3) on the bottom layer. This organic amorphous polymer layer increases the Li-ion diffusivity and avoids damage based on its flexibility and the inorganic LiF - Li_2CO_3 layer contributes to forming the ordered Li nucleation and prevents side reactions by preventing contact between the electrolyte and Li metal^[76,77].

SEI mechanical properties

When some mechanical damage or breakage occurs at the weak natural SEI of Li metal electrodes, the Li metal suffers severe loss of its passivation layer, resulting in the degradation of cell performance. In some cases, thermal runaway can arise at some local points on the electrode. In considering cell design, in addition to its ionic conductivity, the mechanical properties of the SEI are some of the primary factors. Recently, Xia and co-workers characterized the SEI layers in carbonate- and ether-based electrolytes with the aid of a cryogenic electron microscope^[78]. Each organic component was determined during Li plating and stripping. From density functional theory calculations, a single SEI component derived from different electrolytes was predicted. The authors found correlations between the SEI components and mechanical properties and argued that carbonate-based electrolytes are preferable.

Recently, detailed electro-chemo-mechanical modelling was implemented using the finite element method to provide beneficial information for the SEI. The aim was to determine the correlation between the mechanical properties of an artificial SEI and Li deposition. The results showed that the mechanical properties of the SEI are governed by uneven Li deposition, such as in whiskers, tresses, globules and dendrites^[79]. If the ionic conductivity of the SEI is improved, reaching a certain level, mechanical stress cannot be concentrated, resulting in even Li deposition. However, [Figure 5](#) shows that, except for polyvinylidene difluoride, a critical value ($\sigma_{\text{SEI}}/\sigma_{\text{Electrode}}$) of > 0.1 was not found. According to their calculations, a Young's modulus (E_{SEI}) of 4 GPa as a threshold value is a critical point for the deposition of uniform Li growth. Therefore, the ionic conductivity of an artificial SEI needs to be improved without degradation of its mechanical strength. We need to find an artificial SEI to meet the conditions of the threshold values of $\sigma_{\text{SEI}}/\sigma_{\text{Electrode}} > 0.1$ and $E_{\text{SEI}} > 4 \text{ GPa}$. This is a new strategic method of testing artificial SEIs on other metallic anodes^[80].

Solid electrolytes

In spite of the various attempts to suppress dendritic Li growth in liquid electrolytes, unexpected growth still constantly occurs. As a principal solution to replacing liquid electrolytes, many studies are underway to suppress dendritic growth by utilizing solid electrolytes. As shown in [Figure 6A](#), when a liquid electrolyte is used in a Li metal battery, an SEI is formed due to side reactions, and subsequently, the low ionic conductivity of the SEI leads to dendritic Li growth. In contrast, using solid electrolytes with adequate mechanical properties minimizes dendritic growth^[81]. Note that the electrochemical performance of the battery is inferior to that of the liquid electrolyte due to the lack of ionic conductivity, as shown

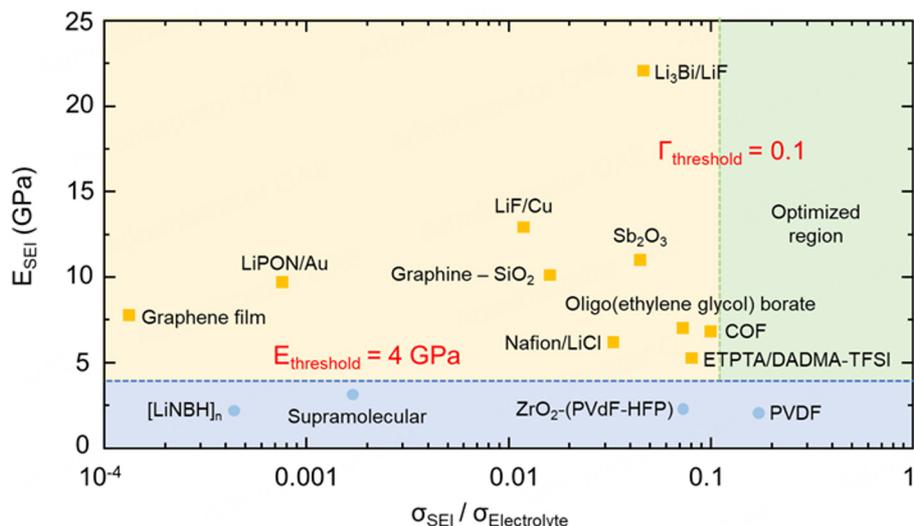


Figure 5. Design guidelines for artificial SEIs to inhibit dendritic Li growth. The yellow and green regions inhibit dendritic Li growth. The threshold values of $\Gamma_{\text{threshold}} = 0.1$ and $E_{\text{threshold}} = 4$ GPa are marked by green and blue dotted lines, respectively. Reproduced from Ref.^[80] with permission from Wiley.

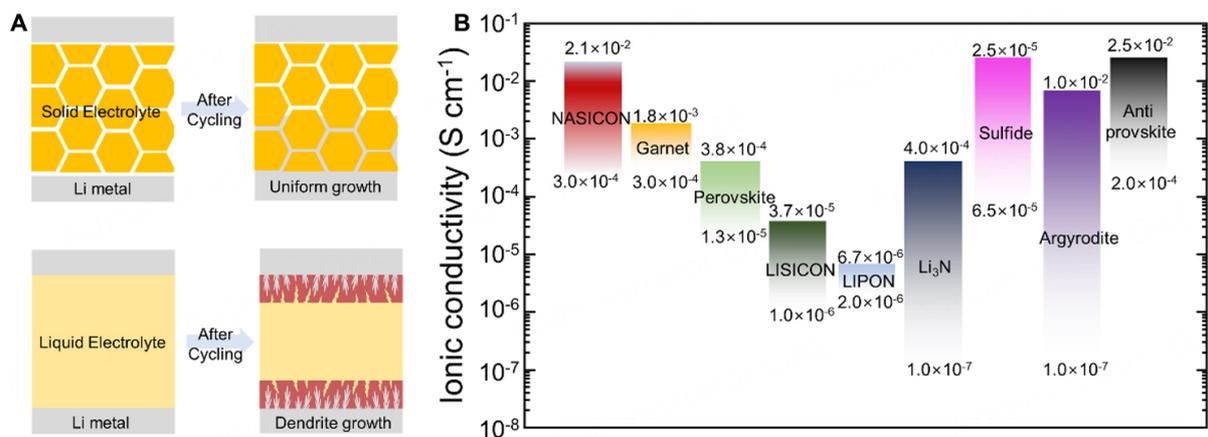


Figure 6. (A) Schematic illustration of dendritic Li growth in solid and liquid electrolytes. (B) Li-ion conductivity in various types of solid electrolytes. Reproduced from Ref.^[82] with permission from Elsevier.

in Figure 6B. To further improve the ionic conductivity in the solid electrolyte, various structures have been tested. It is well known that solid electrolytes can be classified as sodium superionic conductors (NASICONs), garnets, perovskites, lithium superionic conductors (LiSICONs), lithium phosphorus oxynitride (LIPON), Li₃N, sulfides, argyrodites and anti-perovskite structures.

The argyrodite type with the formula Li₆PS₅X (X = Cl, Br or I) has attracted significant attention among the solid electrolyte candidates because of its high ionic conductivity and stability at the Li metal interface. The argyrodite-type solid electrolyte spontaneously reacts with moisture, however, and generates toxic H₂S gas^[82]. To reduce the generation of H₂S, Cho and co-workers proposed a natural zeolite as a functional additive^[83]. To investigate the effect of zeolite nanoparticles, pristine Li₆PS₅Cl and zeolite embedded Li₆PS₅Cl were exposed to humid air (relative humidity (RH) = 50%). The initial ionic conductivity values were estimated to be 1.31×10^{-3} and 1.27×10^{-3} S cm⁻¹, respectively. After exposure for 1 h in humid air conditions

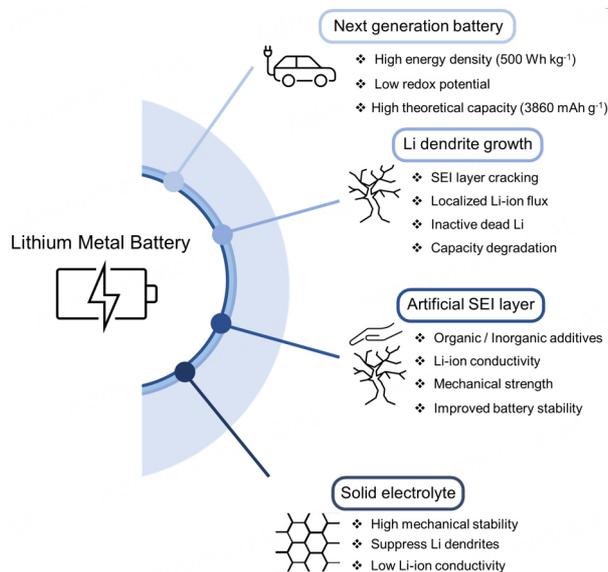


Figure 7. Schematic summary of the Li metal battery focusing on its advantages, dendritic Li growth, artificial SEI layers and solid electrolytes.

(RH = 50%), the Li-ion conductivity of the pristine $\text{Li}_6\text{PS}_5\text{Cl}$ was $0.23 \times 10^{-3} \text{ S cm}^{-1}$, while the zeolite embedded $\text{Li}_6\text{PS}_5\text{Cl}$ was $0.39 \times 10^{-3} \text{ S cm}^{-1}$. The decrease in ionic conductivity was reduced in the zeolite-embedded $\text{Li}_6\text{PS}_5\text{Cl}$ because the continuous contact between H_2O and $\text{Li}_6\text{PS}_5\text{Cl}$ was significantly reduced, since porous zeolite nanoparticles adsorb H_2S and H_2O effectively in their porous structure.

PERSPECTIVE AND OUTLOOK

Enormous research and development efforts have been focused on batteries since they are the energy storage devices of many electronic devices and have become ubiquitous in our daily lives. Ultimately, consumers are demanding electronic devices with high-capacity and lightweight batteries. To meet these requirements, it is necessary to construct batteries using Li metal as the anode, which has advantages such as high theoretical capacity and energy density and low oxidation potential. To commercialize these attractive Li metal batteries, however, it is necessary to suppress the inevitable growth of Li dendrites. Dendritic Li growth is intensified by localized Li-ion flux through cracks in the SEI. This repeated Li growth creates isolated "dead Li", which dramatically reduces the capacity of the battery. In this mini review, we have summarized the SEI layer, which affects the dendritic Li growth, and focused on electrolyte additives in terms of ionic conductivity, mechanical strength and solid electrolytes as a solution to suppress dendritic Li growth, as summarized in Figure 7. To suppress the growth of Li dendrites, the primary key points are achieving increased ionic conductivity of the SEI layer and improved mechanical stability, which is an inherent property of the SEI. In particular, to utilize Li metal as an anode, it is essential to research additives, which generate SEI components, such as Li_3N and Li_2S . These obtain higher ionic conductivity than other SEI components. In addition to these SEI components, an accurate understanding of bilayers and new research insights into additives compatible with each layer are required.

From the mechanical perspective, the use of solid electrolytes is an essential technique to overcome these technical issues. Solid electrolytes can inhibit dendritic Li growth with their robust mechanical strength. However, they have crucial drawbacks, such as low ionic conductivity, compared to liquid electrolytes and contact loss problems with active materials. Argyrodite-type solid electrolytes are emerging as a solution with high ionic conductivity. Note that argyrodite solid electrolytes spontaneously react with moisture in

the air and generate toxic H₂S gas, which is harmful to the human body. To apply them to actual commercial batteries, additives, such as a natural zeolite, that reduce the amount of H₂S gas should be studied. To achieve a Li metal battery with perfect high capacity and stable operation, an in-depth understanding of the SEI is essential. In particular, various SEI components can be generated through chemical additives, so further research on additives with a focus on ionic conductivity and mechanical properties is crucial. As an alternative approach, solid electrolytes can also be a solution if the low ionic conductivity is overcome through atomic substitution and the interfacial problem is solved using coatings.

DECLARATIONS

Authors' contributions

Proposed the topic of this review: Kim JH, Han SA

Prepared the manuscript: Park S, Chaudhary R, Qutaish H

Collectively discussed and revised the manuscript: Moon J, Park MS, Kim JH

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

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Consent for publication

Not applicable.

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