

Electrolyte Design for Low Temperature Lithium-Sulfur Battery: From Different Polysulfide Conversion Mechanisms

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With the increasing demand for large-scale energy storage devices, lithium-sulfur (Li–S) batteries have emerged as a promising candidate because of their ultrahigh energy density (2600 Wh kg^{-1}) and the cost-effectiveness of sulfur cathodes. However, the notorious shuttle effect derived from lithium polysulfide species (LiPSs) hampers their practical application, especially at low temperature. Therefore, electrolytes with low viscosity and high conductivity are required with the advancement of next-generation Li–S batteries. Understanding the interface structure dependent solvent electrochemistry and recognizing the existing issues relating to electrolytes are indispensable prerequisites. This review briefly summarizes the challenges to further develop the new generation of Li–S

batteries, which can operate steadily at subzero temperature, including LiPSs accumulation, Li_2S nucleation, lithium deposition, and so on. On the basis of the crucial role of electrolytes in solving these questions, we outline the corresponding electrolyte design strategies from the different mechanisms (solid-liquid-solid conversion, all-solid-phase conversion, and all-liquid-phase conversion) such as lithium salt modification, additive introduction, and introduction of strong cationic electrolytes, as well as the application of solid-state electrolytes, and so on. Finally, we emphasize promising strategies and solutions to improve low-temperature performance, pointing the way for the future development of maximizing extreme-temperature electrolytes toward practical applications.

1. Introduction

The energy system is the foundation of the national economy, the cornerstone of the functioning of society as a whole, and a key area for achieving climate goals. Since the Industrial Revolution, energy development has been closely related to population and economic growth, so the demand for energy storage systems is increasing rapidly.^[1–3] Lithium-ion batteries, widely used at this stage, are limited by inherent theoretical capacity and actual energy density which cannot meet higher-level requirements in the future. Nowadays, it is urgent to develop a new generation of energy storage systems that can better satisfy market demand.^[4–7] As the high performance and efficient secondary batteries, lithium-sulfur batteries (Li–S) with ultrahigh theoretical energy density (2600 Wh kg^{-1}) and theoretical specific capacity (1675 mAh g^{-1}) have attracted more and

more researchers' attention.^[8–10] And it is generally believed that Li–S batteries can expand the energy density of current commercial lithium-based devices to more than 500 Wh kg^{-1} .^[11–13] Hence, they are very promising used in the field of electronic products, electric vehicles and grid-scale storage and space explorations and other utilizations. However, it is a tough challenge to meet high-performance requirements under extreme climatic conditions, particularly low temperature. For example, different batteries technologies were used in National Aeronautics and Space Administration (NASA) missions, and to further explore the outside of the solar system, the development of a long-term dependable energy storage system with high specific energy density and strong low temperature operation capability has become an urgent task.^[14] Among those multitudinous campaigners, Li–S batteries occupy an absolute prominent position.^[15]

For traditional lithium-ion batteries, long-term exposure in low temperature environment will limit their intrinsic thermal kinetic energy and decelerate the diffusion process of lithium ions.^[16,17] Even worse, gelid weather may cause the common carbonate-based electrolyte to freeze in lithium-ion batteries.^[18] However, 1,3 dioxolane and 1,2-dimethylene oxyethane (DOL:DME, 1:1 v/v) are usually used as electrolyte solvents for Li–S batteries, which ensures smooth operation in a low temperature environment due to their high ionic conductivity of $>4 \text{ mS cm}^{-1}$ at -40°C and low freezing points, -95°C and -58°C , respectively.^[19–21] Unfortunately, the performance of Li–S batteries suffers from significant attenuation under low temperature conditions.^[22] That is the discharge capacity will decay severely with the decrease in temperature, which seriously hinders the practical application of Li–S batteries.^[23] To design low temperature Li–S batteries, except for electrolytes' ionic conductivity, the solution strategy can be more from the

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specific low temperature mechanism process. Thermodynamics and kinetics are also limited especially at low temperature, resulting in a reduction in conductivity, which severely restricts its electrochemical performance and safety at low temperature.

To achieve storage devices that adapt to the huge distribution of temperature difference throughout the country and seasonal weather changes, some studies have been carried out on Li–S batteries from battery construction such as adjusting the electrolyte,^[26,27] improving the electrode/electrolyte interface,^[28,29] modifying active materials^[30–32] and discovering suitable catalysts^[17,33] at low temperature. Among the internal construction, electrolyte plays an important role in connecting the anode and the cathode, and is the medium for Li⁺ transmission during cycling, affecting the reaction of interface and controls safety.^[34] What's more, the various properties of electrolytes and cathode materials, are coupling and interaction, which also leads to the process of different mechanisms in different systems.^[35] Early studies had mainly focused on iterative electrolyte engineering, rather than thermodynamic and kinetic investigations on the crucial influences of temperature, to combat the detrimental effect of low-temperature performance.^[35,36] Therefore, the reaction progress of the

mechanism have been classified into three parts, including the conversion of all-solid phase, solid-liquid-solid and all-liquid phase as shown in Figure 1a–c, and the primary issues at low temperature are simply summarized in this article with Li–S batteries (Figure 1d). In addition, the corresponding solutions for different reaction mechanisms have been further illustrated, such as lithium salt modification, additive introduction, and introduction of strong cationic electrolytes, as well as the application of (quasi-)solid-state electrolytes, etc., in Figure 1e. All in all, we emphasize the promising strategies and solutions to boost the low temperature performance from the mechanism of different types of Li–S batteries, from the electrolytes point of view, giving out the direction for maximizing the practical application at extreme temperature.

2. Mechanisms and Challenges of Low temperature Electrolytes of Li–S Batteries

The electrochemical reaction of Li–S batteries involves the complex process of multistep conversion relating multiple



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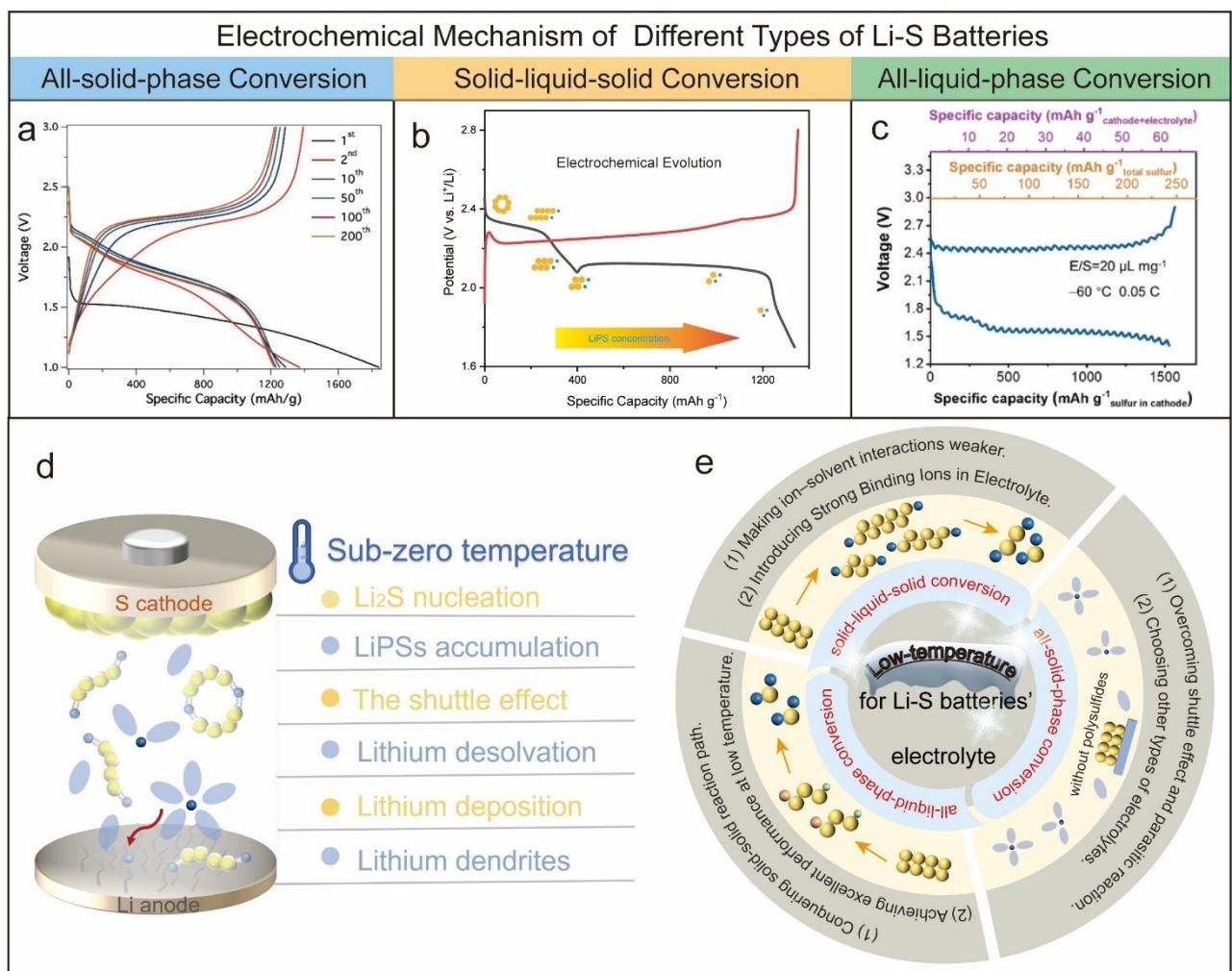


Figure 1. The typical charge/discharge voltage profiles for (a) All-solid-phase Conversion (Reproduced with permission.^[24] Copyright 2015, American Chemical Society), (b) Solid-liquid-solid Conversion and (c) All-liquid-phase Conversion (Reproduced with permission.^[25] Copyright 2021, American Chemical Society). (d) The challenges of electrolytes in Li-S batteries at sub-zero temperature conditions. (e) Strategies of low-temperature electrolytes for Li-S batteries in three conversion mechanism.

electrons, but like other battery systems,^[36–38] the mechanisms of electrochemical performances affected by temperature need to be elaborated from two perspectives: thermodynamics and kinetics. The relevant parameters will affect the capacity of Li-S

batteries, which is summarized in Figure 2. First, the Gibbs free energy (ΔG) is a thermodynamic function introduced to determine the direction of electrochemical reactions. The

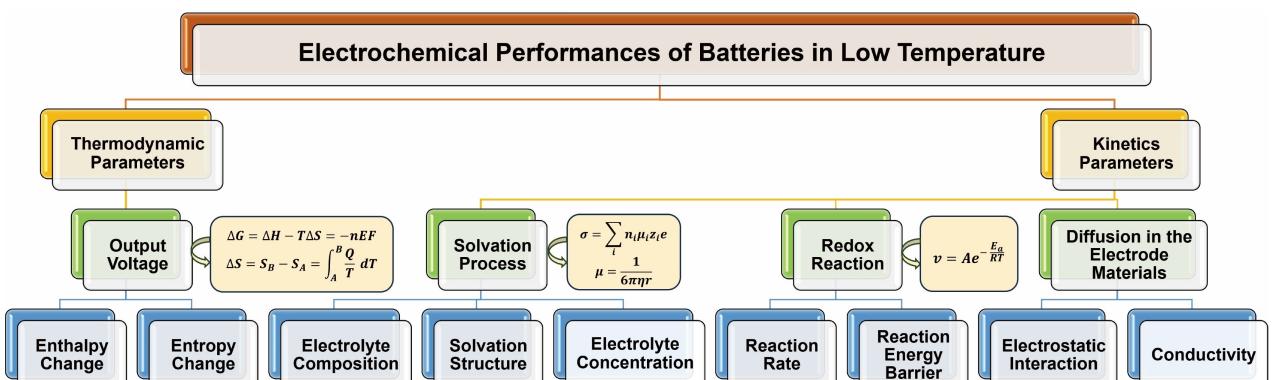


Figure 2. The parameters of mechanisms related to the electrochemical performances of Li-S batteries.

formula of ΔG and entropy change (ΔS) can be defined as follows:^[39]

$$\Delta G = \Delta H - T\Delta S = -nEF \quad (1)$$

$$\Delta S = S_B - S_A = \int_A^B \frac{Q}{T} dT \quad (2)$$

where ΔH is enthalpy, T is temperature, n is the amount of charge in the battery reaction, E is the electromotive force of a reversible battery, F is the Faraday constant, and Q is the heat exchanged during process A to B. Combined with formulas (1) and (2), the output voltage of the battery is related to the system temperature, the enthalpy change, and the entropy change.

From a dynamic perspective, the discharge process of Li–S batteries typically includes the following three stages: (i) The migration process of solvated ions in the electrolyte. During the charging/discharging process, polysulfides can act as a solution medium to achieve charge transfer in Li–S batteries.^[40] This process mainly involves ion migration and diffusion, characterized by the parameter of ion conductivity (σ) and the formula can be expressed as follows:^[41,42]

$$\sigma = \sum_i n_i \mu_i z_i e \quad (3)$$

$$\mu = \frac{1}{6\pi\eta r} \quad (4)$$

where n_i , μ_i , z_i and e is the number of ions, the ion migration number, the charge valence and the unit charge, respectively. η represents the electrolyte viscosity, and r is the radius of the solvated ion. According to formulas (3) and (4), the ion conductivity of the electrolyte is mainly related to the composition, concentration and solvation structure of electrolyte. Low temperature usually causes an increase in the viscosity of the electrolyte, so the low-temperature electrochemical performance of the batteries is often not ideal. (ii) The redox reaction on the electrode surface. Li–S batteries exhibit complex electrochemical behavior, especially at low temperatures. In traditional solid-liquid-solid conversion, the solid-solid conversion between Li_2S_2 and Li_2S is the decisive step in the reaction. Usually, solid-phase conversion has slow interfacial reaction kinetics and mass transfer kinetics, resulting in higher reaction energy barriers. The expression between reaction rate (v) and reaction activation energy (E_a) is as follows:^[43,44]

$$v = Ae^{-\frac{E_a}{RT}} \quad (5)$$

where A and R are the frequency factor and the molar gas constant, respectively. From formula (5), it can be concluded that the reaction rate is directly related to the system temperature and that lower the temperature, the slower the reaction rate. (iii) The diffusion process of electrons and ions within the electrode material. The conductivity of the sulfur cathode

material itself and the electrostatic interaction between Li^+ and the sulfur cathode material play a major role in this process. This procedure will not be elaborated in depth because it mostly involves the reaction kinetics of electrode materials, which are not directly connected to the electrolyte here.

As we know, the electrolyte viscosity will increase or even freeze as the temperature decreases, which seriously hinders the ion migration and material behavior and worsens the performance of Li–S batteries. To address this issue, researchers are exploring additives and novel electrolyte formulations that remain fluid at lower temperatures.^[27,45,46] Furthermore, the shuttle effect of polysulfide also plays an important role in the fading of the capacity at low temperature.^[47,48] Additionally, the electrochemical behavior at low temperatures differs significantly from that at room temperature, affecting the overall efficiency and lifespan of the batteries. And these behaviors include LiPSs accumulation,^[49–51] Li_2S nucleation,^[52,53] lithium deposition^[54–56] and so on. In battery construction, the main functions of electrolytes are conducting working ions to ensure the charge and discharge process of batteries, which are closely related to the kinetic process. To require high low-temperature performance of Li–S batteries, understanding the electrolyte chemistry is an indispensable part. In this section, we outline the main challenges faced in recent research, which will be helpful in providing scientific insight into the exploitation of cryogenic electrolytes.

2.1. The Accumulation of LiPSs

The accumulation of LiPSs is a critical issue in Li–S batteries, leading to decreased battery efficiency and lifespan. Due to the complex electrochemical reaction in Li–S batteries, soluble Li_2S_8 , Li_2S_6 , Li_2S_4 , and insoluble Li_2S_2 , Li_2S are derived. Among them, soluble polysulfides can act as a solution medium to promote charge transfer and generate a rapid and thorough sulfur redox reaction in solution during cycling.^[57] At the time of discharging, LiPSs dissolve and expose the interior of sulfur particles that are not easily touched by electrons and ions, thus improving the utilization rate of sulfur.^[48] A similar effect will occur during the charging process, in which the chemical balance of the polysulfide species helps to catalyze Li_2S oxidation by overcoming the activation energy of LiPSs nucleation.^[49] That is to say, they can regulate the electrochemical conversion process to control the electrochemical performance of Li–S batteries when dissolved and shuttled in liquid electrolyte. However, this behavior results in a heavy decrease in active material when LiPSs shuttle back and forth between electrodes, called the “shuttle effect”, leading to irreversible capacity loss, continuous anodic corrosion, electrolyte decomposition amplification, and low sulfur utilization.^[58,59] And the precipitations of insulating $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ have resulted in a loss of porosity of the cathode and separator, producing by LiPSs the reaction of disproportionation.^[53] These behaviors lead to slow ion migration and increasing cell impedance. Furthermore, the conversion rate of the multistep reaction is inconsistent between liquid to liquid, solid to liquid, and solid to solid. This difference

causes a large amount of soluble LiPSs to exist in the electrolyte. Driven by intramolecular interactions and thermodynamic stability, apart from individual polysulfides, LiPSs tend to aggregate in groups as shown in Figure 3a, especially at low temperatures,^[50,51] seriously restricting the kinetics of electrochemical conversion.

Because of the lower internal energy of formation, the chain-like sulfur clusters are much easier to exist than cyclic or chair-like geometries of polysulfide anions by computational calculations. Through classical molecular dynamics and ab initio sub-dynamics computations, Murugesan's group^[47] has revealed the kinetic processes of lithium polysulfide species, analyzed the spectrum properties of polysulfide clusters, and used experimental and computational NMR and XAS spectra in Figure 3b. Further mechanistic insights into the low-temperature behavior of Li–S are revealed by Arumugam and his partners,^[50] they have used density functional theory calculations, and nuclear magnetic resonance (NMR) spectroscopy suggests that the Li–S system's unfavorable behavior at low

temperatures may increase the tendency of polysulfides to assemble clusters in solution. Massive aggregation of Li_2S_4 will be accompanied by the production of a robust $\text{Li}^+ \text{S}_4^{2-}$ bond network, limiting further development of Li_2S species, since the key kinetic limitation step is the conversion of dissolved polysulfide molecules into solid precipitates. Afterward, they also explain how the intrinsic mechanism of polysulfide clusters limits the electrochemical utilization of active materials, they discover that the diffusion coefficient of polysulfide decreased sharply due to the appearance of cluster ions, which functionally matched the nucleation and growth rate constants of Li_2S deposition.^[49] The kinetic constraints generated by polysulfide aggregation are unified and linked with the nucleation and growth behavior of Li_2S , which enlarged the understanding of the internal electrochemical chemistry of Li–S batteries. In general, the obtained atomic insights into clustering and lithium exchange kinetics are crucial for predicting and understanding the polysulfide shuttling and nucleation processes that determine the performance of Li–S batteries.

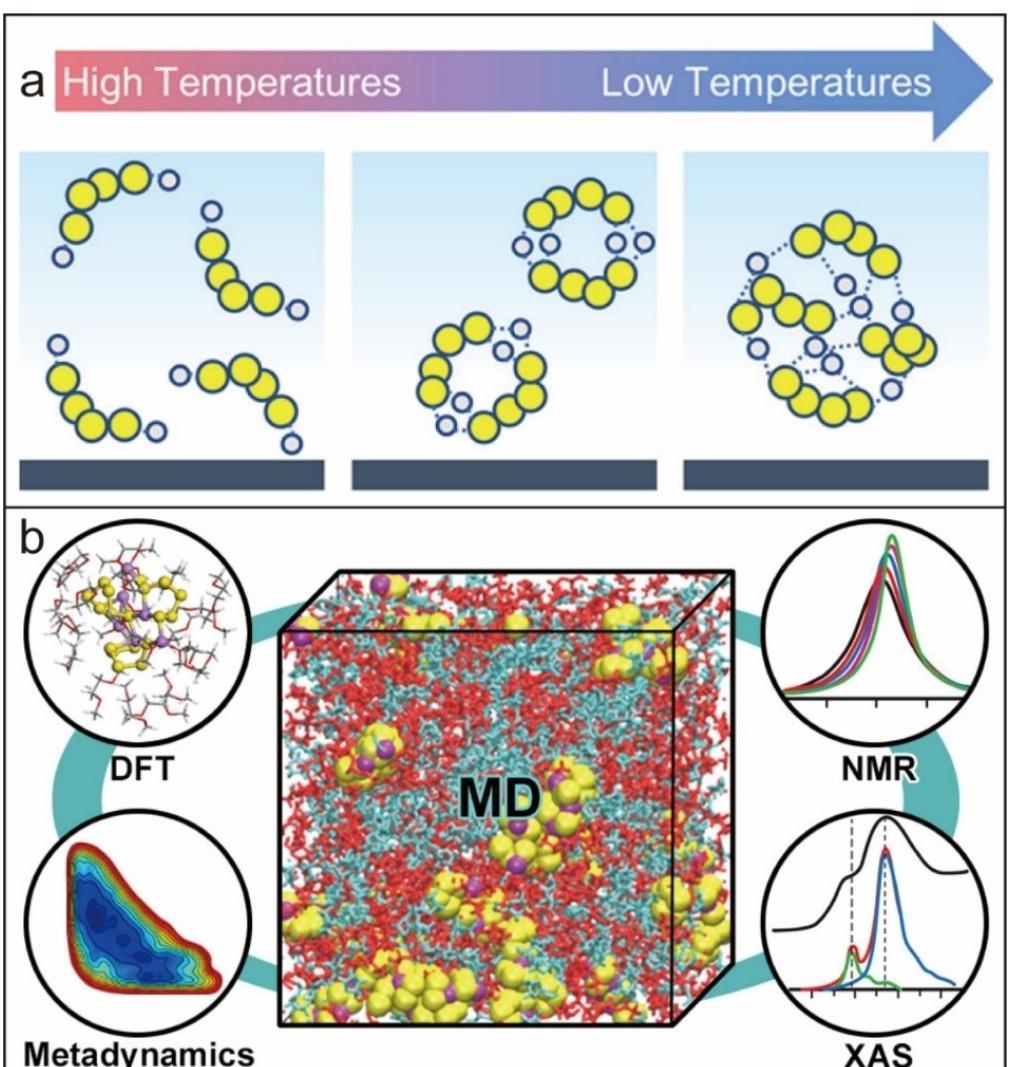


Figure 3. (a) Illustration of the polysulfide ion aggregation when the temperature decreasing. Reproduced with permission.^[50] Copyright 2020, American Chemical Society. (b) Many characteristics means to reveal lithium polysulfide clustering and associate dynamic processes. Reproduced with permission.^[47] Copyright 2019, American Chemical Society.

2.2. The Nucleation and Growth of Li₂S

The nucleation and growth of Li₂S are crucial processes in the performance of Li–S batteries, as they directly influence the battery's efficiency and capacity. Due to limited kinetics, the mechanism of Li–S batteries at low temperature differs from those of room temperature and high temperature environments. The growth tendency of the Li₂S deposit on the electrode plays a significant role in reaction dynamics, especially for the solid conversion from the insoluble Li₂S to S₈.^[60] There are still challenges in controlling the electrodeposition of electrically insulating solid phases, especially at subzero temperature, and it is critical for battery performance to maintain accessible electrode surfaces. Therefore, understanding the controlled process of electrochemical deposition and the mechanism of Li₂S deposition/growth is one of the most necessary steps. The low sulfur utilization and low rate capability result in premature passivation of Li₂S, because the insulating Li₂S deposit will passivate the electrode surface to prevent a subsequent cathodic reaction.^[61,62] What's more, the morphology and structure of solid Li₂S products are the key factors determining the achievable high discharge capacity, the rate capacity, the utilization rate of active materials, and the reversibility of the sulfur material. The growth mechanism of Li₂S deposition and its dependence on the electrode substrate have been extensively studied by theoretical and experimental methods, including scanning electron microscopy (SEM) imaging and atomic force microscopy (AFM).^[63–65] The recent study on the regulation of Li₂S deposition behavior was discussed based on the modified composition of the electrolyte, surface chemical control of the sulfur host and catalyst design, but the electrodeposition of Li₂S is controlled by electrode kinetics, Li₂S solubility, and polysulfide/Li₂S diffusion,^[66,67] which are determined by the solubility, polarity and viscosity of the solvent, respectively. Therefore, the optimization of the electrolyte to adjust the intrinsic chemistry of Li₂S growth is the basic solution to achieve high sulfur utilization and high low temperature performance.

Based on the complexity of the sulfur cathode and the unique solution-mediated reaction mechanism, the unique behavior at low temperature needs to be explained with the help of a series of theoretical calculations and conclusive experimental evidence. Abruna *et al.*^[63] studied the evolution of the morphology and crystal structure of the sulfur cathode in the Li–S battery by using synchrotron-based X-ray diffraction, microscopy, and tomography. It is found that the position of the sulfur clusters after reformation deviates from their initial distribution and depends largely on the current density and temperature during discharge and recharge, respectively. By synchrotron-based X-ray diffraction (XRD), microscopy, and tomography, the evolution of the morphology and crystal structure of the sulfur cathode in a Li–S battery has been studied. It was discovered that the positions of the sulfur clusters after reformation deviated from their initial distribution and were primarily influenced by the temperature and current density during discharge and recharge, respectively.

As different temperatures decrease to 5 °C, the size of sulfur and Li₂S particles tends to form smaller nanoscale clusters in Figure 4a. Helms *et al.*^[53] have displayed electrodeposited Li₂S as a porous 3D deposit on the carbon current collector during battery discharge, thus improving the utilization of sulfur in Figure 4b. The effect of the BPI redox mediator on the redox reaction of Li–S also affects the nucleation and growth process of Li₂S. Furthermore, Kim *et al.*^[69] reported that particulate lithium sulfide growth can be achieved using a salt anion with a high donor number, such as bromide or triflate in Figure 4c. As shown in these reports, the deposition of nanoscale particles can be considered as film-like growth (2D growth), while the larger clusters suggest the more ideal 3D growth.^[53,63,69] That is to say, the 2D growth is more likely to bring about the passivation of the cathode in contrast to these two growth mechanisms, because of hindering electron transfer and not taking full advantage of active material,^[65,70] which also elaborates the reason for poor low-temperature performance.

2.3. Lithium Deposition

Lithium deposition is a critical factor affecting the performance and safety of lithium-based batteries, particularly in terms of capacity and cycle life. The low redox potential of lithium (Li) metal (3.040 V) makes it almost compatible with all positive electrode materials. In addition, the ultra-high theoretical specific capacity of 3860 mAhg⁻¹ makes lithium metal always regarded as the most potential negative electrode material.^[55,71] However, lithium metal is prone to the growth of lithium dendrites during charging and discharging, especially at very low temperatures.^[72] More notably, the morphology of Li deposition changes from bulk to needle-like as the operating temperature decreases, which accelerates electrolyte consumption and premature battery failure.^[56] To make matters worse, needle-like dendrites are more likely to pierce the separator, causing a short circuit or even explode of the battery. What's more, if the high-LiPSs (soluble) clusters at low temperature are much more difficult to convert into low-LiPSs (insoluble) in time, a large number will accumulate in the electrolyte and diffuse to the negative metal lithium electrode through the separator under the effect of concentration gradient.^[73] It will react with the metal lithium and deposit on the negative electrode surface, resulting in the reduction of active sulfur and further affecting reaction kinetics.^[67] Furthermore, the deposited lithium tends to form smaller particles, like Li₂S growth in a cold environment, which makes it easy to grow "dead lithium" and leads to the significant reduction of Coulombic efficiency.^[66] To overcome the inherent defects under low temperature conditions, there are some related research directions based on relevant influencing factors:

- (1) The uneven nucleation of lithium is caused by the uneven concentration distribution of lithium ions at the lithium anode interface. When the moving speed of lithium ions is less than the speed at which they are reduced at the electrode interface, lithium ions at the interface cannot be replenished in time after they are reduced, and lithium-ion

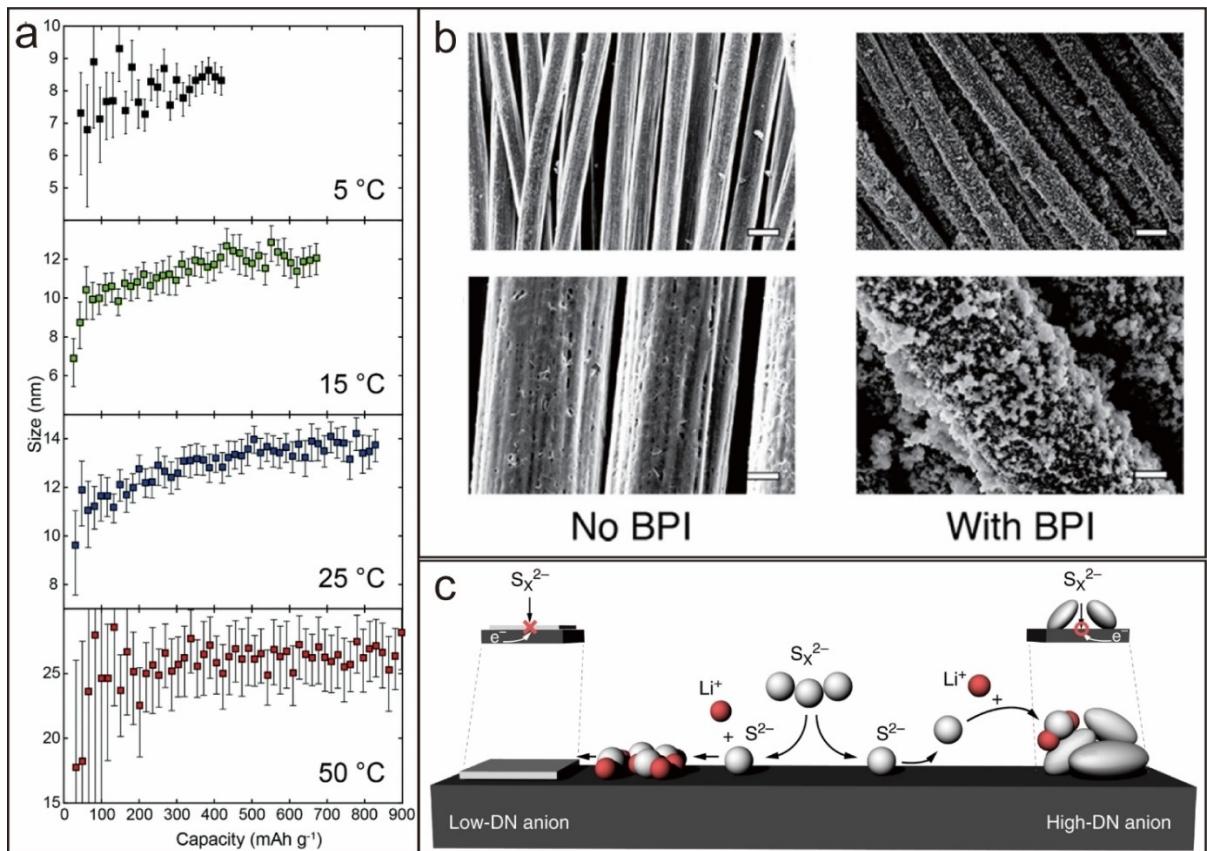


Figure 4. (a) The particle size of Li₂S calculated by (111) Bragg peak at different temperature. Reproduced with permission.^[63] Copyright 2020, Royal Society of Chemistry. (b) SEM images of Li₂S deposited without BPI and with BPI. Reproduced with permission.^[53] Copyright 2015, American Chemical Society. (c) Mechanisms for the different lithium sulfide growth behaviors in the electrolytes of low-donor number anions and high-DN anions. Reproduced with permission.^[68] Copyright 2020, Wiley-VCH.

depletion regions will appear in the electric double-layer region, which will lead to very uneven nucleation of lithium ions. Therefore, improving the concentration and distribution uniformity of lithium ions at the lithium electrode interface is expected to promote the uniform nucleation of lithium ions and inhibit the generation of lithium dendrites.

- (2) The solid electrolyte interface (SEI) layer has poor mechanical properties, unevenness, and poor compactness. The ultrahigh electrochemical reaction activity makes lithium metal inevitably react with electrolytes at the electrode interface, forming a porous solid electrolyte interface (SEI) layer on the electrode surface.^[54,72] The composition of the SEI layer comes mainly from the solvated layer of lithium ions, which contains organic components generated by the decomposition of solvent molecules and inorganic substances produced by the decomposition of lithium salt and electrolyte additives. The uniform SEI of different components distribution leads to the inhomogeneous nucleation of lithium and induces lithium dendrite. To gain a dense, stable SEI layer, is important for releasing the detriment of lithium dendrite in electrolyte engineering.

As a type of lithium metal anode battery (LMB), a Li–S battery also suffers from some similar problems at low temperature, including uneven lithium dendrite growth, unstable SEI

film, and additional consumption of electrolytes. In general, it is necessary to control the morphology and structure of the deposited Li to avoid the formation of Li dendrites on the surface of the Li anode, which forms dense and stable SEI films for high-performance Li–S batteries.^[74] To overcome the inherent defects of lithium metal anode materials at low temperature, some research has revealed that the structure, chemistry and transport characteristics of SEI are strongly influenced by temperature. For example, In Figure 5a and b, McDowell *et al.*^[56] found that the morphology of the deposited lithium changed significantly and the different structure, chemistry, thickness and conductivity of SEI exhibited as the temperature decreased by low temperature transmission electron microscopy combined with vacuum transfer X-ray photoelectron spectroscopy. On the basis of the DOL/DME/LiTFSI system, SEI formed at a lower temperature is thinner, and has lower resistance compared with SEI formed at room temperature. Cui and his colleagues^[75] also explore the temperature-dependent behavior of lithium metal in ether-based electrolytes in Figure 5c. D. Abruna *et al.*^[76] visualize the evolution of lithium plating/stripping used by the synchrotron-based X-ray imaging method, which demonstrates the effects of key battery operating parameters on lithium plating/stripping, including lithium salt concentration, current density, ionic strength, various electro-

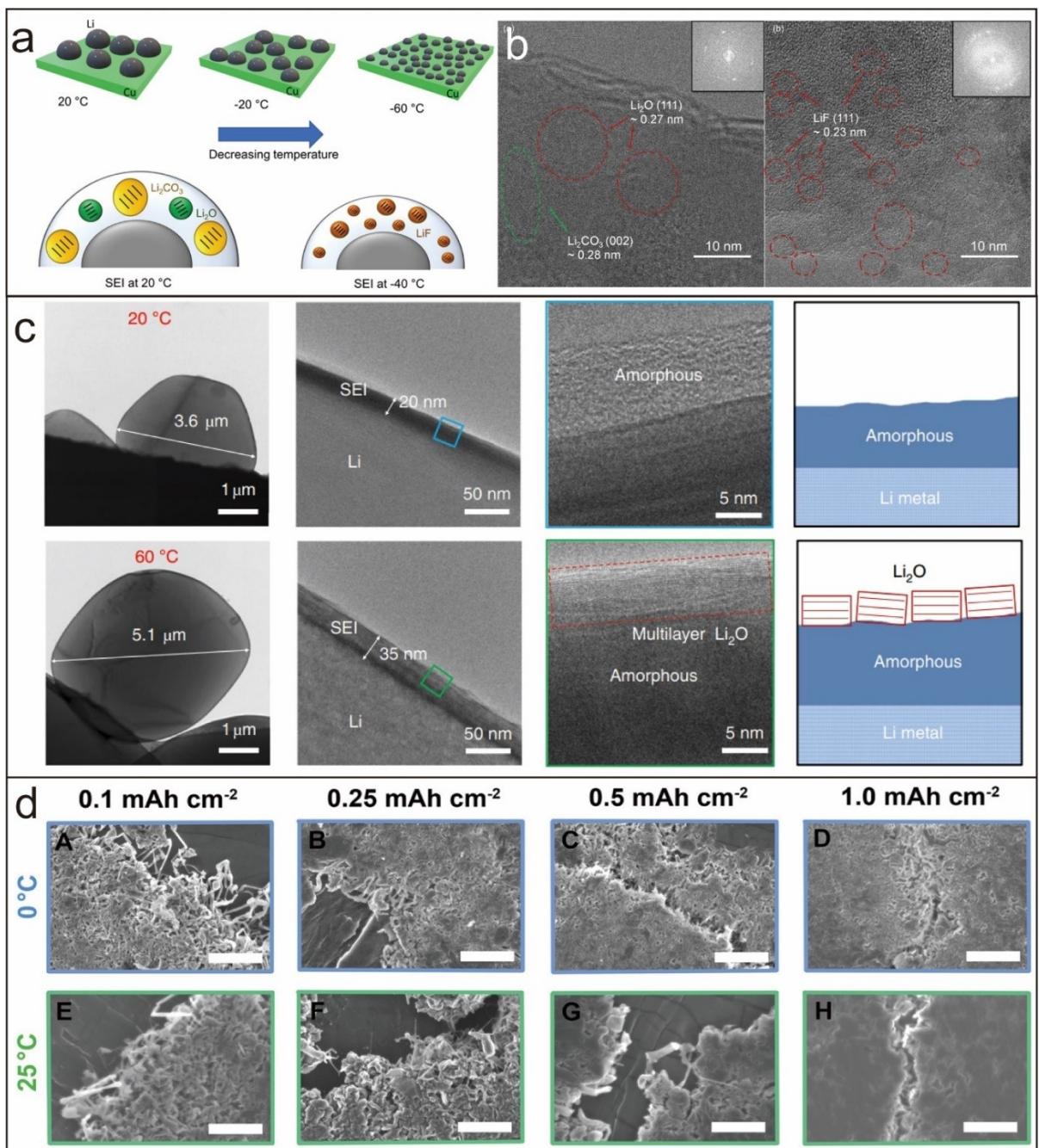


Figure 5. (a) Schematic diagram of temperature-dependent SEI decreasing temperature from 20 °C to –60 °C. (b) The SEI structure visualized with cryo-TEM micrographs at 20 °C and –40 °C, respectively. Reproduced with permission.^[56] Copyright 2019, American Chemical Society. (c) The SEI structure revealed by cryo-electron microscopy in DOL/DME at 20 °C and 60 °C. Reproduced with permission.^[75] Copyright 2019, Springer Nature (d) SEM images of the Li metal growth on surface at different temperature, 0 °C and 25 °C. Reproduced with permission.^[68] Copyright 2020, Wiley-VCH.

lytes and additives. In other words, electrolyte composition has a great influence on the electrochemical behavior of a lithium-metal anode. Sun *et al.* investigated the temperature-dependent behavior of the lithium anode visually observed by SEM images in Figure 5d, and then described its electrochemical behavior and failure mechanism. After understanding these mechanisms of Li–S batteries facing an extreme environment, we will summarize different coping strategies according to

specific situations and point out research directions in the next research.

3. Electrolyte Design at Low Temperature from Different Polysulfide Conversion Mechanisms

The previous reviews of electrolyte engineering strategies are mainly based on lithium salts, solvents, additives, etc. However, the polysulfide clusters, the growth of Li_2S deposition and serious lithium dendrite pose new challenges for low temperature Li–S batteries' electrolytes. Therefore, it is necessary to expound them from the different conversion mechanisms. The corresponding solution strategies in different mechanisms will be put forward in the following electrolyte design, which can achieve the maximum low temperature performance at present and point the way for future development under a subzero climate.

3.1. Solid-Liquid-Solid Conversion

Solid-liquid-solid conversion is a key mechanism in the operation of lithium-sulfur (Li–S) batteries, whose electrochemical process is different from the classical intercalation/deintercalation mechanism of transition metal oxides, based on Li_2S_x

($3 < x < 8$) undergoing a solid-liquid-solid redox transformation process.^[77] The above conversion can be described as follows:

- (1) During the discharge process, Li^+ derived from metal lithium combines with solid sulfur (S_8) to form soluble polysulfides ($\text{S}_8 \rightarrow \text{Li}_2\text{S}_8 \rightarrow \text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S}_4$), and its voltage platform is approximately 2.3 V, corresponding to 25% of the theoretical capacity is 418 mAh g^{-1} .
- (2) The long-chain polysulfides (Li_2S_4) are reduced by the electrochemical deposition mechanism. Finally, the short-chain Li_2S is precipitated back onto the electrode ($\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_2 \rightarrow \text{Li}_2\text{S}$) with a voltage plateau of 1.9–2.1 V, which contributes 75% of the theoretical capacity (1225 mAh g^{-1}) of the remaining sulfur.^[40,78,79]

As described above, the main capacity is made up of the second step of the "solid-to-solid" process of S_4^{2-} to S^{2-} , in which the reduction of insoluble intermediates (Li_2S_4 and Li_2S_2) presents large barriers for cryogenic Li–S batteries due to the inherent sluggish kinetics of the solid-solid reaction, causing a significant capacity reduction. On the contrary, as shown in Figure 6a there is only an obvious long platform about 2.3 V during the charging process, consistent with the oxidation of Li_2S to elemental S_8 ($\text{Li}_2\text{S} \rightarrow \text{S}_8$).^[81] However, through the redox process mediated by the polysulfide solution, the severe shuttle

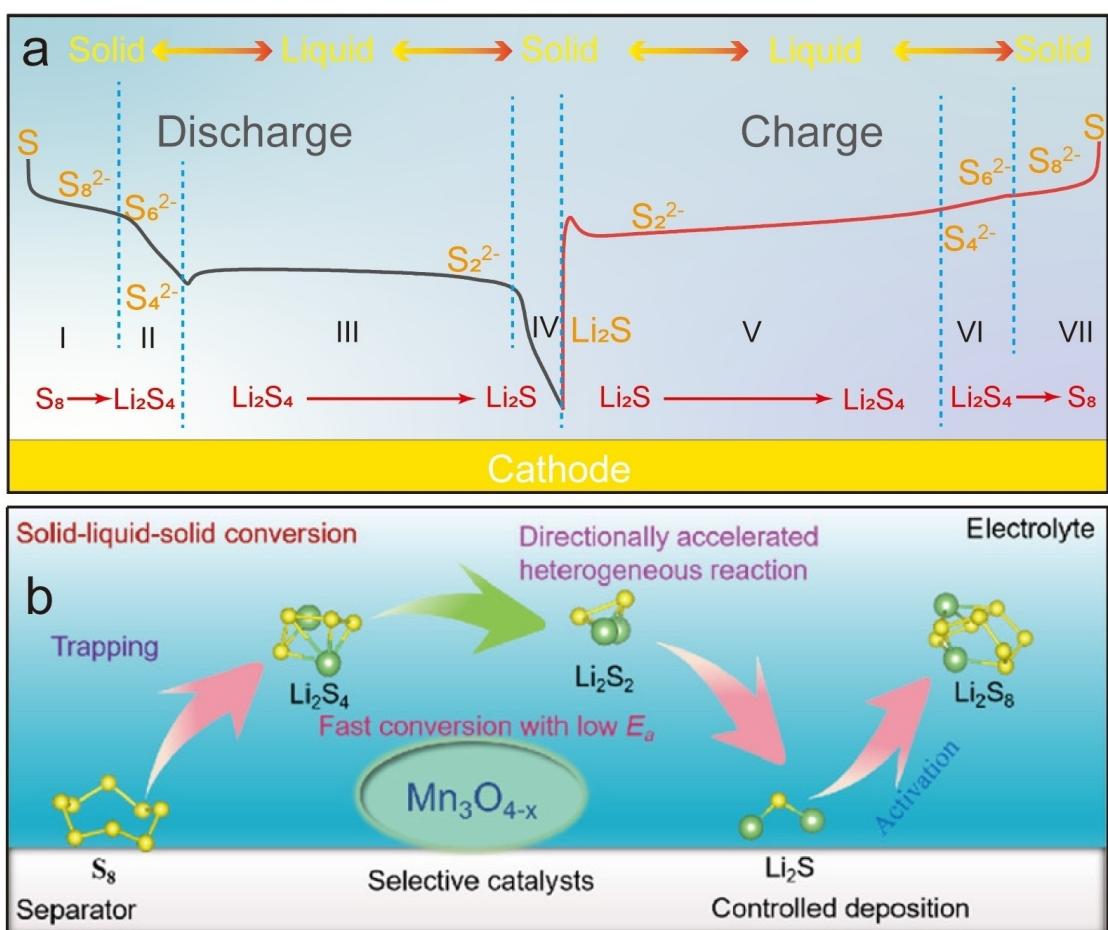


Figure 6. (a) Solid-liquid-solid conversion of representative charge and discharge curve and the variation of LiPS. (b) Schematic for the process of solid-liquid-solid conversion with selective catalysts. Reproduced with permission.^[80] Copyright 2022, Wiley.

effect of soluble polysulfides and harmful side reactions cause rapid capacity fading and short cycling life. Whereas the shuttle effect of polysulfides is equivalent to internal short circuit, it not only causes serious corrosion of the lithium anode, but also affects battery self-discharge, resulting in poor cycle performance and low Coulomb efficiency, which seriously hinders the research and development of lithium-sulfur batteries.^[33,82] Hence, in view of the current understanding of the mechanism of low temperature Li-S battery, we can begin destroying the accumulation of polysulfide, influencing the Li_2S desolvation and deposition process. The research methods are summarized as follows:

3.1.1. Making Ion-Solvent Interactions Weaker

The solvated structure of lithium ions in the electrolyte has a significant impact on the performance of the electrolyte. The accurately regulated solvated structure of lithium ions in Figure 7a and b can stabilize the electrode interface of lithium batteries and improve the working performance of the electrolyte under extreme conditions.^[83,84] The formation of Li^+ solvation sheath is a competition between cation-anion, cation-dipole and dipole-dipole interactions,^[85,86] like in Figure 7c. Recently, by modifying the polarity of the solvent,^[87,88] adjusting the concentration and type of lithium salt in the electrolyte,^[27,89]

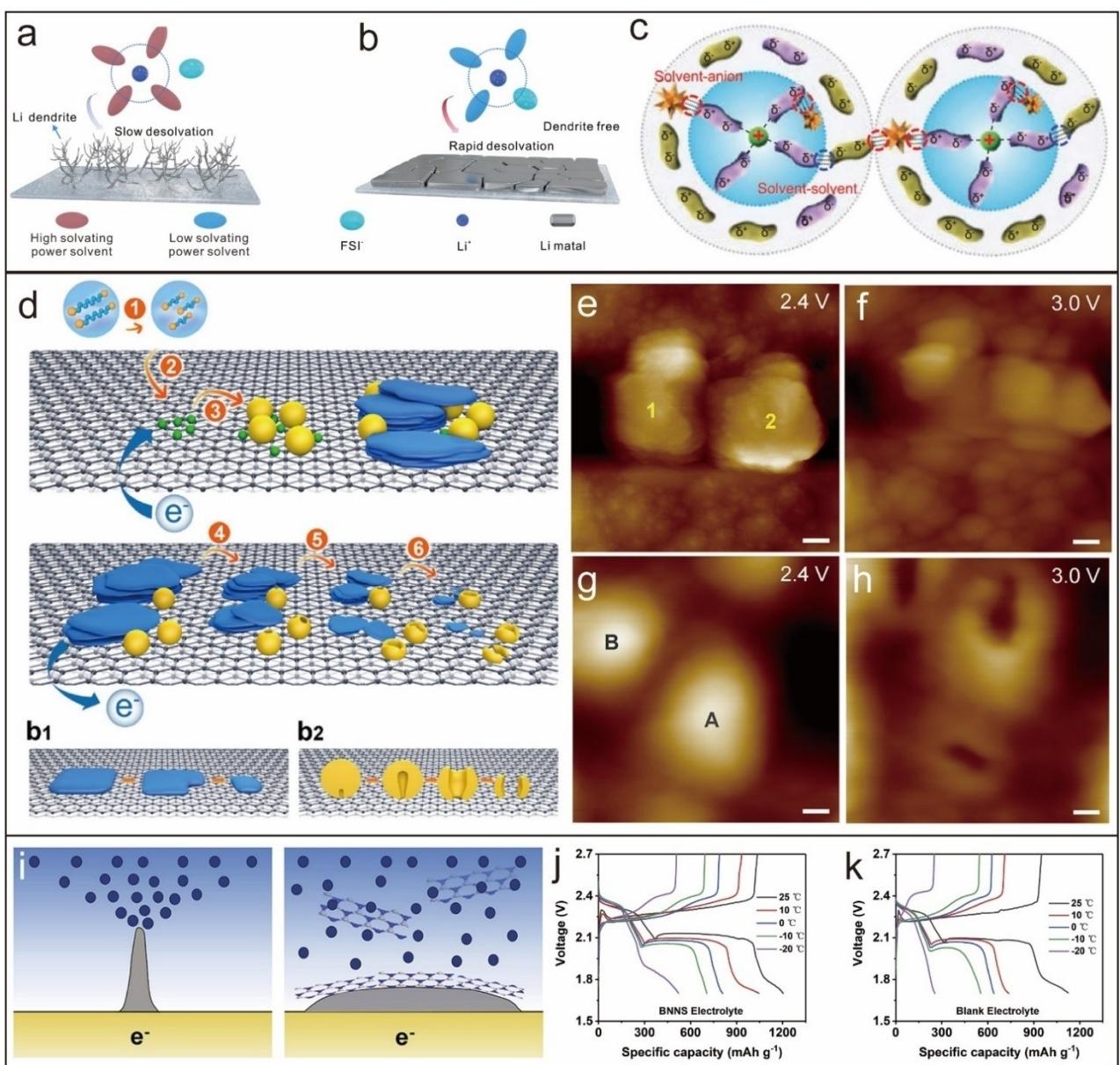


Figure 7. Effect of electrolyte structure on lithium deposition morphology (a) in slow desolvation and (b) in rapid desolvation. Reproduced with permission.^[84] Copyright 2022, Wiley-VCH. (c) Schematic formation of solvent-anion pair and solvent-solvent pair during Li^+ solvation. Reproduced with permission.^[96] Copyright 2022, Wiley-VCH. (d) Schematic sulfide reactions at electrode interface in LiTFSI-LiFSI binary salt electrolyte. In-situ AFM characterization of Li_2S decomposition, in which (e,f) lamellar in LiFSI-based electrolyte and (g,h) spherical in LiTFSI-based electrolyte. Reproduced with permission.^[97] Copyright 2018, American Chemical Society. (i) The addition of BNNS can flatten Li deposition differ from Li dendrites. The charge/discharge profiles of Li-S cells display at various temperatures in (j) the BNNS electrolyte and (k) the blank electrolyte. Reproduced with permission.^[90] Copyright 2020, Elsevier.

or introducing additives with coordination functions,^[90,91] the components of the lithium ion solvated structure can be controlled, so that anions and additives participate in the lithium ion solvated structure, thus improving the inorganic components of the electrode interface phase, or changing the binding energy of the solvent and lithium ions, accelerating the desolvation process of lithium ions and reducing the transmission impedance of the battery.^[92,93] The interactions between anions and cations, solvents, cosolvents, and additives can change dynamically throughout the complex electrolyte system, which brings us great difficulties in analyzing the behavior of electrolytes. Fortunately, advanced characterization methods and computational simulations have been developed to analyze Li⁺ solvation structures to study the behavior of electrolytes. Next, the mechanism that affects the solvation is analyzed from the adjustment of solvent, lithium salt, and additive.

3.1.1.1. Regulation of Solution

As we know, the resistance and kinetic barrier of Li⁺ will increase at low temperature. To reduce these resistances, the usefulness of low freezing point solvents is an essential strategy for improving the low temperature capability of Li–S batteries, including 1, 3dioxolane (DOL), 1, 2- dimeth oxyethane (DME), tetra(ethylene glycol) dimethyl ether(TEGDME) and so on.^[94] Besides, the desolvation energy of lithium ions depends mainly on the coordination ability and coordination number of solvent molecules in the solvent shell of lithium ions.^[84,85] However, it can not only affect the formation and composition of the SEI, but also impact the energy barriers associated with desolvation at the Li⁺ electrolyte/electrode interface. This affects the lithium deposition behavior, especially at low temperatures. In weak-solvation energy electrolytes, the lithium ions desolvation process is easier due to the weaker ability of solvent molecules to associate with lithium ions.^[95] Therefore, the development of electrolytes with weak-solvation energy is eagerly anticipated to alleviate rapid capacity fading and safety issues in low-temperature Li–S systems.

The inherent characteristics of the solvent have a non-negligible relationship with its solvation behavior. Hassoun *et al.*^[98] demonstrate the effect of chain length on species mobility in the electrolyte, which directly affects the behavior in Li–S batteries based on the properties of glyme solvents of various molecular weights. D. Abruna *et al.*^[94] found that the use of lower viscosity ether solvents resulted in a more complete reduction of soluble polysulfides, which were more readily oxidized in viscous ether solvents, utilizing *in situ* sulfur K-edge X-ray absorption spectroscopy (XAS). Later, Lu and Zou^[99] revealed that the Li–S redox reaction in high-donor number solvents (such as dimethyl sulfoxide (DMSO)) and low-donor number solvents (such as DOL, DME) undergoes different chemistries through Operative UV-Vis spectroscopy, in which the stability of the polysulfide intermediates involved is different, and these precisely determine the reaction rate of the polysulfides disproportionation/dissociation/complexation. For example, using high-concentration dimethylformamide solvent

exhibits stronger S3[−] stability compared to dimethyl sulfoxide and significantly reduces Li–S cell polarization. Therefore, the solvent with a short chain, low viscosity, and high donor number is more conducive to the construction of a weak solvated structure, accelerates the diffusion of Li⁺, and reduces the charge transfer energy, effectively improving the conversion mechanism of low-temperature lithium-sulfur batteries.

Because of the weak solvation binding of solvent molecules, the problems of insufficient dissociation of lithium salts and low lithium-ion conductivity require other solvents with high dielectric constant to improve the solubility of lithium salts and the ionic conductivity. In 2003, Mikhaylik and Akridge^[23] demonstrated that low temperature performance as low as –40 °C can be improved by using the DOL: DME ratio of 86: 14 in the electrolyte instead of the more traditional 1:1 volume ratio. Therewith, Liu *et al.*^[100] studied the effect of adding 1,3-dioxolane (DOXL) and methylacetate (MA) to the electrolyte formula mainly containing tetra(ethylene glycol) dimethyl ether(TEGDME), which showed a beneficial improvement in low temperature performance compared to pure TEGDME electrolyte. Li group^[55] also indicated that the coordination interaction between Li⁺ and TEGDME is higher than that between Li⁺ and 1,2-dimethoxyethane (DME) or 1,3-dioxolane (DOL) by density functional theory calculations combined with Raman spectroscopy. This result verified that the aforementioned pure TEGDME electrolyte had poor performance. These solutions help form a protective layer on the electrode, extending its life under ambient conditions. However, the protective layer hinders the ion intercalation kinetics at low temperature. Most cosolvents fundamentally improve the ion transport properties of the cathode surface, but at the expense of increasing anode-electrolyte interfacial resistance.

To improve irreversible lithium plating at low temperature, the modification of solvent molecules can optimize the morphology and structure of the SEI layer to achieve high coulombic efficiency for lithium (Li) metal batteries. Chen *et al.*^[87] showed that cyclic carbonates and ethers can significantly improve the coulombic efficiency of Li metal anodes at low temperature (–60 °C) to tune the solid electrolyte interface (SEI) structure. However, most of the current fluorination modification solvents are concentrated in ester and carbonate, and polysulfides only have parasitic reactions with these solvents, so they are not suitable for systems with such a conversion mechanism. To avoid the occurrence of polysulfides, we have introduced the all-solid-phase conversion, which is a good way of generating the LiPSs. The subsequent chapters will then summarize this method in detail.

3.1.1.2. Anion Regulation

Due to the unique solid-liquid-solid conversion mechanism, the lithium salts used in traditional low-temperature lithium-ion batteries, such as LiPF₆, LiBF₄, LiBOB, LiBF₂C₂O₄, are not necessarily suitable for Li–S batteries.^[23,89,91] Although the factors influencing the type of lithium salt and solvent have been studied in the early stage of Li–S batteries, the interfacial

mechanism of the dynamic evolution of its chemical reaction is not very clear. Recent studies have shown that the anion-related properties of lithium salts are directly related to the Li₂S deposition morphology at the cathode/electrolyte interface in Li–S electrochemical reactions, while lithium salts can control ion diffusion and interfacial reactions.^[101] What's more, Kalra *et al.*^[102] found that changes at molecular-level of salt anions occurred in electrolytes to response to PS speciation, which was monitored by attenuated total reflection (ATR) in situ FT-IR. These results provide insight into the dynamic interactions between electrolyte salts and polysulfides. More importantly, lithium salts can further control the viscosity, electrical conductivity, and solvent interactions in the electrolyte to control the different Li–S kinetics of multistep polysulfide reactions. Therefore, rational selection or design of electrolytes is crucial to controlling the detrimental shuttling reaction and protecting the electrode surface.

Early research focused on exploring suitable lithium salts for application in low-temperature lithium-sulfur systems. In 2003, Mikhaylik and Akridge^[23] optimized the salt type and solvent concentration by comparing electrolytes with different lithium salts, such as LiSCN, LiSO₃CF₃, and LiN(SO₂CF₃)₂, dissolved in the hybrid solution of dimethoxyethane (DME) and 1,3-dioxolane (DOL), with the intention of achieving high electrochemical activity of polysulfide on at the low discharge plateau. In 2005, Park and his partners^[103] used mixed imidazolium salts and lithium salts for the electrolytes investigated as a means to improve the low temperature performance. However, it is essential to understand these internal mechanisms. Wan *et al.*^[97] successfully disclosed the path of Li₂S growth in different salt environments used by in-suit AFM monitoring in Figure 7d–h, which mediates the interface structure and kinetic behavior of Li₂S cathode and then the performance of affects Li–S batteries. Besides, the said Li₂S films were observed in low DN solvents, while flower-like Li₂S particles were grown in medium and high DN solvents. Although sulfur utilization could be improved when solvents with high Gutmann donor numbers were used, lithium metal corrosion was more severe. Kim *et al.*^[69] found that salt anions with high donor numbers (such as bromide or triflate) also induced 3D particle growth of Li₂S and improved the chemical conversion between Li₂S and soluble PS anions, allowing full utilization, without severely deteriorating Li metal electrodes.

Because lithium salts and lithium polysulfides share the same cation of Li⁺, the concentration of the former has a significant effect on the dissolution of the latter in the electrolyte. To further understand the ionic speciation and transport properties in various concentration ranges, the significant performance of the battery has been reported by adjusting the amount of salt in the electrolyte. Garcia-Araez *et al.*^[104] reported conductivities and viscosities in the molar concentration range of 10⁻⁵ to 5, based on lithium bis(trifluoromethanesulfonyl)imide in 1,3-dioxolane electrolyte as a model system, concluded that triplet ion formation was responsible for the highest molar conductivity values, followed by a maximum at 1.25 M. Furthermore, it has also been found that although reducing the electrolyte salt concentration

reduces the ionic conductivity, sulfur utilization and rate performance of Li–S batteries are found to benefit from this process. Gan *et al.*^[105] replaced LiTFSI with less dissociable salts (LiI, LiBr) to reduce the free Li⁺ in the electrolyte, which would reduce the electrolyte salt concentration and increase the saturation point of Li₂S₂/Li₂S. Several products not only delayed the insulation of the formation of the cathodic conductor network layer, but also improved the conversion efficiency of dissolved lithium polysulfides to Li₂S₂/Li₂S. Latest, Wu *et al.*^[27] employed a low concentration electrolyte (LCE, 0.1 M) to accelerate the Li–S conversion reaction and suppress the shuttle effect of polysulfides at low temperature, resulting in higher capacity utilization and more stable cycling performance at –20°C. In conclusion, the optimal solvent/salt ratio is crucial to controlling solubility and conductivity, and the appropriate electrolyte concentration in different systems still needs to be explored.

3.1.1.3. Addition Regulation

Due to the significantly increased charge transfer resistance and decreased Li⁺ conductivity at subzero temperatures, the severe growth of Li dendrites will become more uncontrolled.^[56] In addition, lithium metal with high chemical activity can reduce almost all lithium salts and solvents. The formation of a solid-state electrolyte interface (SEI) can effectively mitigate these negative behaviors. And the most common way to alleviate the problem is to use additives, making the SEI film more uniform and denser.^[106,107] If not, SEI with a heterogeneous structure can lead to nonuniform deposition of lithium. Simultaneously, it is also unable to adapt to drastic volume changes, which promote repeated cracking/repairing of SEI, depletion of lithium metal/electrolyte, and eventually the formation of lithium dendrites.^[108]

To form a relatively stable solid electrolyte interface film at the interface between the lithium anode and the electrolyte, some methods have been developed to suppress the harm caused by dendrites. For example, inspired by the choice of leveling agents in conventional electroplating to achieve dendrite-free metal deposition, Huang *et al.*^[90] showed 2D boron nitride nanosheets (BNNSs) as liquid electrolyte additives to flatten Li protrusions and achieve dendrite-free lithium metal anode in Figure 7i. Among them, B atoms act as Lewis's acid sites to interact with Lewis basic anions in the electrolyte, reducing the Li⁺ concentration gradient, improving the ability of Li deposition, and achieving 43.3% of the room temperature capacity in Li–S batteries at a low temperature of –20°C (Figure 7j). The blank electrolyte only retained 22.06% in Figure 7k. In addition, M. Oh *et al.*^[109] added a small amount of allyl sulfide as an electrolyte additive in Li/Graphite cells, increasing the reversible capacity of graphite electrodes up to three times that of AS-free cells at –30°C.

Recently, the robust SEI formation has been the main focus of additives focused on film-forming additives. Using lithium nitrate (LiNO₃) as an additive is the most effective way to prevent side reactions, Fu *et al.*^[107] achieved the preferential

reduction of LiNO_3 and the formation of inorganic-rich SEI in carbonate electrolytes by introducing pyridine as a new carrier solvent, greatly improving the enhance its reversibility. However, LiNO_3 has poor thermal stability, and strong hygroscopicity is easy to explode after friction, which is not conducive to large-scale industrial applications. Lai *et al.*^[110] proposed zirconium oxynitrate ($\text{ZrO}(\text{NO}_3)_2$) as a bifunctional electrolyte additive. They found that the NO_3^- anion can not only contribute to the formation of a stable passivation film, but also catalyze the conversion of dissolved polysulfides to S_8 , trap dissolved polysulfides and prevent them from diffusing into the electrolyte phase. However, the existence of additives in Li–S tends to adversely affect energy density, internal resistance, and cycling stability. Usually, the double-salt electrolyte system can act as a donor of lithium ions, and facilitate the formation of a smoother and denser surface of the lithium anode. Among them, lithium borate with good thermal stability (such as lithium tetrafluoroborate) (LiBF_4), lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalate)borate (LiDFOB), etc., has been reported. Cui *et al.*^[89] proposed that the addition of lithium difluorophosphate (LiPO_2F_2) addition can significantly improve the cycling performance and the rate capability of NMC/Li) batteries at -40°C . A novel electrolyte composed of ethyl 1,1,2,2-tetrafluoroethyl ether (ETFE), conventional ether 1,3-dioxolane (DOL), and the film-forming additive LiFSI was applied in Li–S batteries by Du *et al.*^[111] in which the addition of LiFSI promotes ion conduction, reduces the solubility of polysulfides in the electrolyte, and improves the compatibility of the electrolyte with metallic lithium.

However, the use of additives in Li–S tends to adversely affect the energy density, internal resistance, and cycling stability, and additive-free methods to form robust SEIs have not received enough attention. S. Ozkan *et al.*^[112] develop an additive-free regulation technology for the formation of SEI of specific voltage platforms of Li–S batteries, which can be completed by one to three cycles of slow discharge/charge (C/20-C/100). The current is calculated from the information collected by customizing the model electric vehicle, and finally characterizes the robust SEI formation to enhance cycle performance.

3.1.2. Introduction of Strong Binding Ions in Electrolyte

The material chemistry of Li–S batteries is dependent on the unique behavior of the soluble lithium polysulfide intermediate, which regulates the charge transfer process in the electrolyte during charging and discharging. Lithium polysulfide is surrounded by solvents and salt compounds, which is the key way to make full use of sulfur active materials in electrochemical reactions.^[113,114] Lithium polysulfide tends to cooperate with other polysulfide units in the solution to form large clusters, especially at low temperature and poor electrolyte conditions, which will hinder the process of electrochemical conversion.^[51] On the other hand, the electrochemical contribution capacity of Li–S batteries mainly depends on the solid-solid conversion in the second step, in which at low temperature the original poor

kinetic process will be further limited, and a large number of polysulfides will accumulate in the liquid phase as in Figure 8a, increasing the degree of agglomeration.^[49] There is an effective method to suppress this harmful aggregation behavior, that is, to destroy the properties of polysulfide clusters, to improve the dynamics chemistry of Li–S batteries at low temperature.

In recent work, researchers have revealed that the introduction of strong binding ions in electrolytes can provoke competing electrostatic interactions in solution.^[49,50] Here, this strategy shows that the presence of strongly bound ionic substances with electrostatic competitive interaction with Li^+ or S_x^{2-} will affect the tendency to aggregation, to prevent the formation of clustered $\text{Li}^+ \text{--} \text{S}_x^{2-}$ bond networks in Figure 8b and c. Arumugam and his partners^[50] explained that the strong electrostatic attraction between highly negative anions and lithium ions in lithium trifluoroacetate (LiTFA) hinders the coordination of adjacent polysulfide units and results in the more favorable kinetic behavior at low temperature. The association energy value of Li^+ and TFA^- is much closer to that of lithium polysulfide species, which would prevent the formation of polysulfide clusters to the maximum by boosting the competitiveness with lithium ions. The researchers then sought insight into how to influence the coordination of dissolved polysulfide at low temperature, not just by putting the strong bonding force of the anionic groups into effect. The introduction of strong cationic species, such as NH_4^+ with the abovementioned TFA^- in solution, has shown that the in-suit conversion of NH_4TFA and lithium polysulfide converts to diammonium polysulfide to prevent the formation of adverse polysulfide aggregates through various electrochemical, spectroscopic and computational studies.^[51] Due to the synergistic effect of $\text{NH}_4\text{--}\text{S}_x^{2-}$ and $\text{Li}^+ \text{--} \text{TFA}^-$ as the equation in Figure 8d, the polysulfide networks were broken by introducing strong binding cationic and anionic, enhancing the solution-mediated kinetics in Li–S battery chemistry.^[51] This solution provides a great improvement just by modifying the lithium salt anion, and promotes the development of a cryogenic electrolyte system.

3.1.3. Concentrated Liquid Electrolyte

Compared with traditional diluted electrolytes, high-concentration electrolytes have been a rising star in electrolyte research, which also have been successfully applied in high specific energy batteries. In addition, the concentrated liquid electrolyte has a wide electrochemical window, long cycle stability, and high energy density that traditional electrolytes cannot match.^[118–120] At the same time, applying this concept to a series of electrolyte designs including “solvated ionic liquid”,^[121,122] “super-concentration”,^[123,124] “salt coated solvate”, “salt coated water”^[125,126] or “local high concentration”^[127,128] will help to promote the further development of batteries. However, the development of high concentration electrolyte in low temperature Li–S batteries is not very extensive at present, which also provides broad research space for future development.

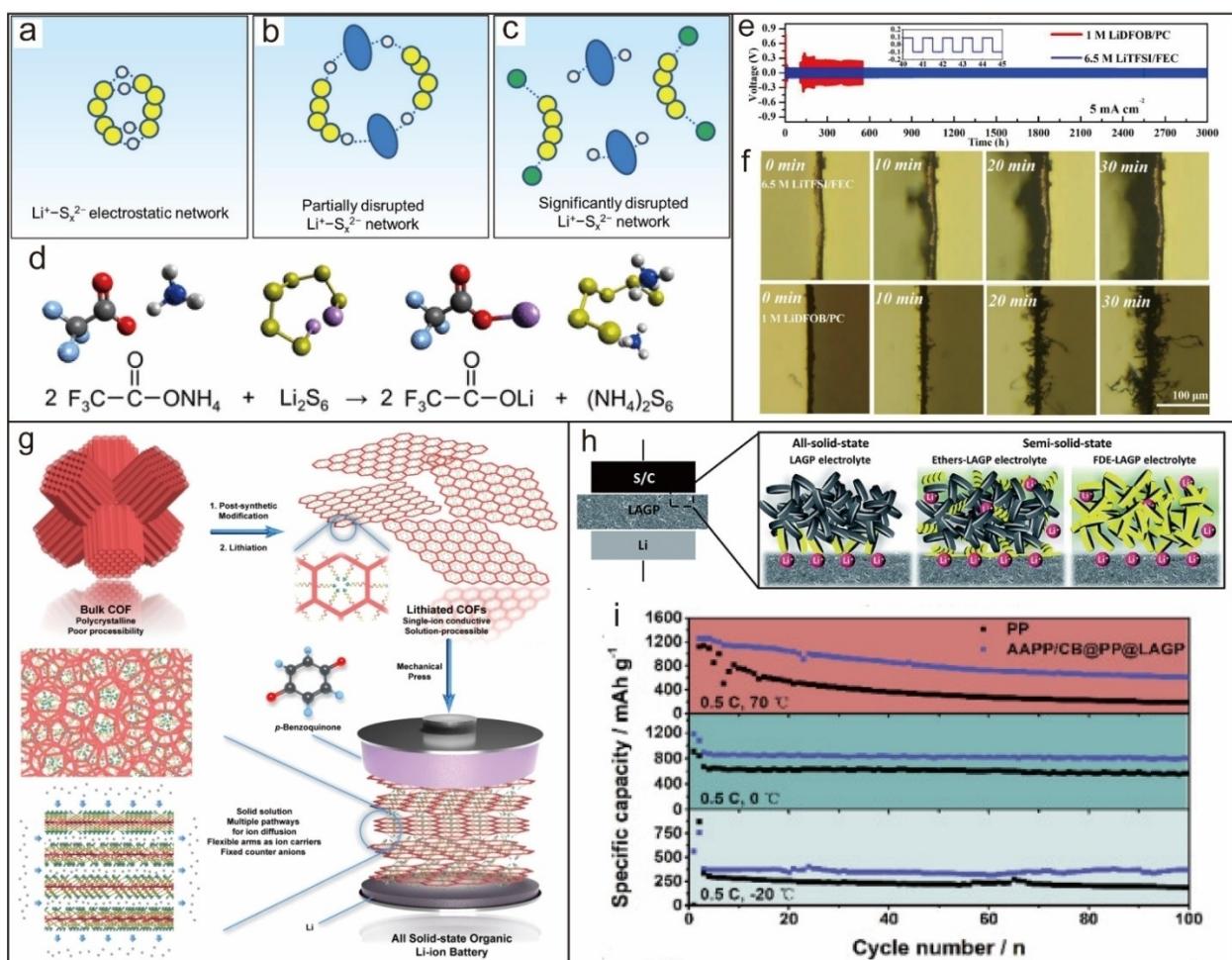


Figure 8. (a–c) Strong $\text{Li}^+ - \text{S}_x^{2-}$ bond networks can be disrupted from competing electrostatic interactions between lithium ions and lithium salt anions. (d) Reaction pathway between NH_4TFA and lithium polysulfides. Reproduced with permission.^[51] Copyright 2021, American Chemical Society. (e) Voltage profiles of Li/Li symmetrical cells. (f) Deposition morphology of lithium-metal to the copper foils using an in situ optical microscope in the Li/Cu half cells with 6.5 M LiTFSI/FEC electrolyte and 1 M LiFOB/PC electrolyte. Reproduced with permission.^[28] Copyright 2020, American Chemical Society. (g) Schematic diagram for the fabrication of lithiated COF nano chips in all solid-state batteries. Reproduced with permission.^[115] Copyright 2020, American Chemical Society. (h) Schematic illustration of the Li–S batteries based on LAGP solid electrolyte (solvent-free LAGP electrolyte) for all-solid-state batteries and liquid-LAGP hybrid electrolytes for semi-solid-state batteries. Reproduced with permission.^[116] Copyright 2017, Royal Society of Chemistry. (i) High and low temperature cycling performances at 0.5 °C, 70 °C, 0 °C and -20 °C. Reproduced with permission.^[117] Copyright 2020, Elsevier.

Due to the rapid increase of viscosity and the apparent decrease in molar conductivity at higher concentrations, high-concentration electrolytes do not seem to work well at low temperature. However, the interaction between lithium ions and anion can be reduced due to the charge delocalization of anions using a low-dissociation lithium salt, including LiTFSI. In addition, the participation of aprotic Lewis bases, such as the strong coordination of ether oxygen atoms and Li^+ in DOL, contributes to the dissolution of lithium salt. Coupled with its unique low dielectric constant, it is conducive to the formation of neutral ion pairs, thus reducing the molar conductivity of all concentrations except the extremely dilute concentration. Cui and several colleagues^[104] designed a concentrated flame-retardant electrolyte including 6.5 M LiTFSI/FEC, which was developed for wide temperature Li–S batteries at -10 °C, 25 °C, and 90 °C. This prepared non-flammable concentrated electrolyte not only expressed excellent flame retardancy and high

lithium-ion transfer number (0.69), but also stable lithium-ion plating/stripping behavior (2.5 mah cm⁻² over 3000 hours) in Figure 8e. Otherwise, attributed to the LiF-rich solid electrolyte interface (SEI), the continuous growth of lithium dendrites was greatly inhibited in Figure 8f, which showed the superior performance of Li–S batteries. It is worth noting that although the low temperature condition will further limit its kinetic energy, it can not only ensure sufficient lithium salt, but also alleviate the shuttle effect of polysulfide. We can continue to explore an appropriate liquid electrolyte concentration to prevent the solution of polysulfide, which may weaken the trends of polysulfide clusters and realize long-term application at low temperature.

3.1.4. Solid-State Electrolyte

The effective development and large-scale application of new energy technologies will bring revolutionary changes to the global energy pattern.^[129] Among numerous emerging energy storage systems, the solid state Li–S battery is expected to improve the safety performance and energy density of the battery. And due to its significant advantages such as high safety, low cost, and high specific energy, it is considered that one of the most promising large-scale energy storage devices.^[130–132] The method using liquid electrolytes suffered from the shuttle, which capacity attenuation was still observed. In addition to the solid-liquid-solid conversion, the solid-state electrolyte (SSE) can effectively solve the shuttle effect of polysulfide, because the solid-state ceramic with a high Li⁺ transfer number can completely suppress the contact between a lithium anode and an intermediate polysulfide (S_n²⁻). However, many realistic problems need to be solved in practical applications, for example, the ionic conductivity is lower and the interface resistance is higher, especially at low temperature, which limits the electrochemistry performance of Li–S batteries.

In order to enhance the ion conductivity of the solid-state framework at low temperature, single-ion conductors have been developed to be convenient for the transportation of Li⁺. Kian Ping Loh *et al.*^[115] demonstrated the use of hydrazone COF as a solid electrolyte (SE), which achieved that at –40°C the ion conductivity reached 10⁻⁵ S cm⁻¹ and the transference number of Li⁺ is 0.92. Such excellent low temperature properties of SE are attributed to the existence of ordered one-dimensional (1D) channels in the covalent organic framework (COF) and the stability against phase transition (Figure 8g). Kang, collaborating with his partner,^[133] obtained excellent single-ion conductive electrolytes by anchoring large anionic groups on the metal organic framework (MOF), which can effectively inhibit the formation of lithium dendrites. These research methods and ideas provide guidance for Li–S batteries in exploring the sustainable operation of low-temperature solid electrolytes. What's more, the hybrid electrolyte with ceramics and liquid electrolytes has been used in Li–S batteries, which based on maintaining the advantages of SSE, conductivity can be continuously improved. Qian *et al.*^[116] used NASICON oxide ceramics and fluorinated electrolytes as semisolid electrolytes, and the unique function of the LAGP-FDE combination in Figure 8h allowed the Li–S batteries to have excellent retention of capacity and long-term stability, in which it retained 668 mAh g⁻¹ after 1200 cycles and delivers superior endurance at –5°C. Wei *et al.*^[117] designed a double-sided structure of ammonium alcohol polyvinyl phosphate/carbon black (AAPP/CB) based on the “ion guide agent” of Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) on a polypropylene (PP) substrate, which the modified separator delivered the discharge capacity of 372.2 mAh g⁻¹ after 100 cycles even at terrific –20°C, while the capacity of 189.5 mAh g⁻¹ with only PP separator in Figure 8i. This combination, like the above-mentioned mixed electrolyte, indicates that ionic conductors play an important role in improving low temperature performance. In addition to the materials presented, solid electrolytes also include super electronic sulfide,

and lithium thiophosphate conductors, which have a high ionic conductivity of 3.01 mS cm⁻¹ at room temperature. But there have been few reports on low temperature.

3.2. All-Solid-Phase Conversion

All-solid-phase conversion is a process in advanced Li–S batteries where the transformation between different lithium-sulfur compounds occurs entirely in the solid state, without the involvement of liquid phases. As a representative of all-solid phase conversion, sulfurized pyrolyzed poly(acrylonitrile) (SPAN) is a sulfur-containing cathode material with non-dissolution mechanism, which was first prepared and published by Wang *et al.* in 2002. It is different from carbon-sulfur composite materials with solid-liquid-solid conversion, and the SPAN cathode reacts elemental sulfur with polyacrylonitrile through heat treatment and poly(acrylonitrile) undergoes a cyclization reaction to form a polypyridine ring.^[134] At the same time, sulfur-free radicals are covalently connected to the structure of the polypyridine ring to form the C–S bond and an S–S bond. Unlike the traditional solid-liquid-solid reaction mechanism of lithium-sulfur batteries, there is only a single-phase reaction in SPAN as the sulfur carrier. According to current research progress, it is not difficult to summarize the advantages of SPAN over elemental sulfur:^[135–137] (1) Based on the sulfur mass, its specific discharge capacity can be close to or even higher than the theoretical specific discharge capacity of Li–S batteries, and it is generally believed that the retention rate of capacity of SPAN can reach more than 90% after 100 cycles. (2) Dissolution of long-chain lithium polysulfide in electrolyte is completely avoided, and there is no shuttle effect. (3) SPAN is chemically compatible with the LiPF₆ carbonate electrolyte used in lithium-ion batteries, and the adaptability of its corresponding electrolyte can be learned from the research progress of lithium-ion batteries. (4) The self-discharge rate of the SPAN cathode material is very low and the coulomb efficiency is as high as 100%. As a result of the absence of a traditional liquid phase reaction procedure, the selection of electrolytes is not limited to ethers, which expands the range of electrolyte options. In addition, with the help of an electrolyte engineering strategy, it also has excellent electrochemical performance at low temperature based on the continuous optimization of sulfide polyacrylonitrile electrode materials.

This single-phase solid-solid reaction mechanism can omit the influence of the shuttle effect in the development of low-temperature electrolytes. Unlike the electrolyte selection of traditional Li–S batteries is limited to ethers only, the proposal of all solid-state reaction mechanisms provides the possibility of the application of other types of electrolytes. Chen *et al.*^[87] discovered the all-fluorinated electrolyte containing methyl 3,3,3-trifluoropropionate (MTPF)/fluoroethylene carbonate (9:1), also operated at ultralow temperatures and high voltage. Also, fluorinated derivatives based on ethylene carbonate (EC), fluoroethylene carbonate (FEC), and difluoroethylene carbonate (DFEC) are also used as high dielectric constant solvents under low temperature. In addition, another group^[26] had designed an

ester-based electrolyte for ultra-low temperature cycling in Li-S batteries, which lithium bis(fluorosulfonyl)imide (LiFSI, 1 M) is used as lithium salts and methyl propionate (MP) and fluoroethylene carbonate (FEC, volume fraction 10%) are acted as cosolvent additives to stabilize SEI in Figure 9a and b. When assembled with the SPAN cathode, this electrolyte system expressed high compatibility and offered 78% room temperature capacity retention at -40°C (Figure 9c). A localized high-concentration electrolyte (LHCE), soxazole-based electrolytes were designed by Yang and his partners,^[29] which contained

fluoroethylene carbonate (FEC) as additive and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) as diluent. It had been testified by several advanced characterization techniques in Figure 9d-f, and the high ionic conductivity at low temperature significantly improved the low temperature performance of this system, which displayed 273.8 mAh g^{-1} at -30°C in Figure 9g and the capacity retention reached almost 99.85% after 50 cycles in Figure 9h.^[29] What's more, the addition of fluoroethylene carbonate (FEC) generates new SEI layers

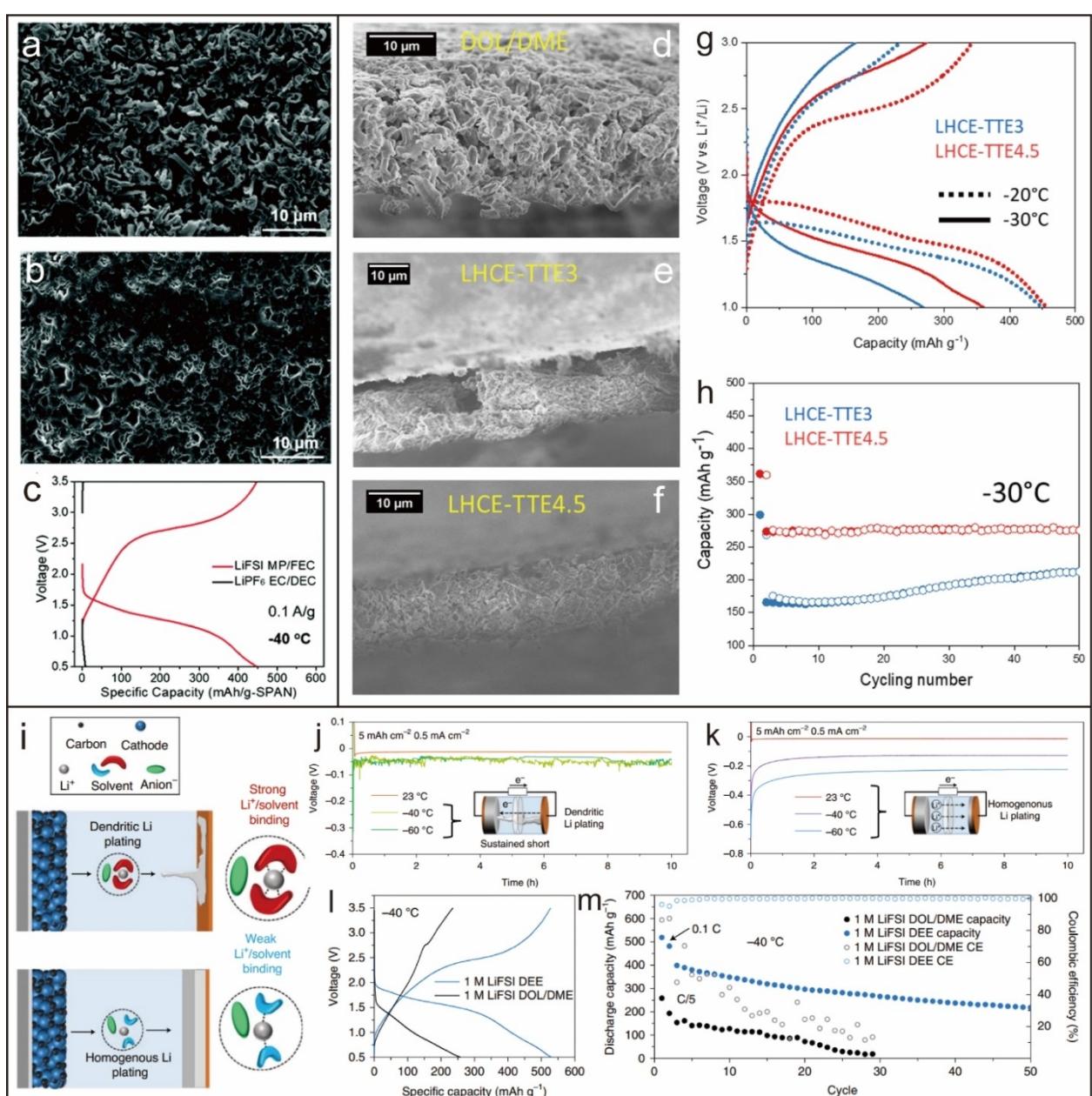


Figure 9. The SEM images of Li deposits obtained in (a) LiPF₆ EC/DEC and (b) LiFSI MP/FEC. (c) -40°C with a current density of 0.1 A g^{-1} in each electrolyte. Reproduced with permission.^[26] Copyright 2020, Royal Society of Chemistry. The SEM images of deposited lithium on Cu foil in Li/Cu cells using (d) 1 M LiFSI in DOL/DME, (e) LHCE-TTE3 and (f) LHCE-TTE4.5. (g) Charge-discharge voltage profile of Li/SPAN cells at -20°C and -30°C and (h) Li-SPAN cycling stability at -30°C using LHCE-TTE3 (blue) and LHCE-TTE4.5 (red). Reproduced with permission.^[29] Copyright 2022, Journal of The Electrochemical Society. (i) Schematic diagram of lithium deposition affected by Li⁺/solvent binding. The characterization of Li deposition profiles (j) in 1 M LiFSI DOL/DME and (k) 1 M LiFSI DEE at 0.5 mA cm^{-2} . (l) Charge/discharge profiles at 0.1 C . (m) Cycling performance at -40°C , respectively. Reproduced with permission.^[95] Copyright 2021, Springer Nature.

abundant with LiF and Li_2CO_3 , which exhibits high electrical conductivity at low temperature.

In addition to methods for solvent modification, ionic solvation can also extend the operating potential window while maintaining ionic conductivity at ultralow temperature. Liu *et al.*^[95] demonstrated the effect of the local solvation structure of the electrolyte on the charge transfer behavior at ultralow temperature (Figure 9i), in which the high-capacity deposition was further implemented to offer characterization at low temperature (Figure 9j and k). When charged and discharged at -60°C , the batteries retained 76% of their capacity using DEE electrolyte, while it is only 2.8% in DOL/DEM (Figure 9l and m). Nazar *et al.*^[138] reduced the solvent/salt molar ratio in the diglyme system (G2:LiTFSI) by adjusting the electrolyte structure. The sulfur reaction pathway is changed from a dissolution-precipitation system to a quasi-solid-state conversion regime, thereby realizing the prohibition of the polysulfide shuttle. These works confirm the importance of the solvated structure for reversibility and electroplating behavior at low temperatures in Li anodes, and also point the way for the design of ultra-low temperature electrolytes.

3.3. All-Liquid-Phase Conversion

All-liquid-phase conversion is a method in Li–S batteries where the redox reactions of sulfur species occur in the liquid phase. This approach facilitates the uniform distribution and mobility of reactants, potentially enhancing the reaction kinetics and overall battery performance. Abovementioned, the solid-solid conversion discussed in detail is mainly divided into two steps. In some published research results, Li–S batteries can completely release the capacity of the first platform at low temperature, because charge transfer in the liquid phase is very easy. The inherent slow kinetics of the solid-solid reaction results in a significant capacity decay at low temperature.^[49] Therefore, the key step is how to improve the oxidation-reduction kinetics in the solid-solid conversion process. The conversion mechanism can be improved by using electrocatalytic active materials in cathode materials and membranes, but the degree of improvement is still limited.^[19,114,139] Inspired by the fact that the first platform can normally release capacity at low temperature, the realization of all liquid reactions can successfully bypass the solid-solid reaction path, and achieve excellent performance at low temperature by greatly reducing the reaction activation energy of the electrode as in Figure 10a. Like a train meets a mountain, the opening of a new tunnel will become a more convenient and fast option. In fact, these soluble intermediates can undergo facile charge transfer in solution, enabling solution-mediated pathways on which Li–S systems are based. Hence, the all-liquid-phase conversion has opened up a new path for the low-temperature Li–S electrolyte. Recently, Yan *et al.*^[25] published that conventional electrolytes added with allyl methyl disulfide (AMDS) additive realized the reaction mechanism of all-liquid-phase to improve the Li–S battery performance at low temperature. In-situ UV-vis, ex-situ ^1H NMR and molecular dynamics (MD) simulations had jointly proved

that sulfur reacted with AMD to turn into trisulfide and then reduced to the Li_2S , which all discharge intermediates were soluble in electrolytes. This all-liquid-phase mechanism successfully avoided the process of solid-solid conversion, and realized a rapid liquid-phase reaction channel, thus bringing about an ultra-high specific capacity of 2408 mAh g^{-1} (sulfur in the cathode) at -40°C by this novel chemistry conversion (Figure 10b) and the cycling capacity at various temperatures (Figure 10c). What's more, Li_2S growth differs from the traditional electrolyte, which is a favorable 3D deposition format in Figure 10d.

4. Summary and Outlook

As the most competitive new-energy candidate, Li–S batteries have been widely studied because of their high energy density. However, most of them are limited to room temperature conditions and are not ideal for extreme climates. In the past two decades of research, great achievements have been made in the development of low-temperature Li–S electrolytes. Herein, by systematically reviewing the challenges faced by low-temperature electrolytes, we have started with polysulfide agglomeration, Li_2S nucleation growth, and lithium deposition, to better understand the reasons for poor performance. In addition, this work summarizes several key coping strategies, including weakening ion–solvent interactions, introducing strong binding ions in electrolytes, and so on. From the mechanism of solid-liquid-solid conversion, all-solid conversion and all-liquid conversion, it is proposed to improve its cycle life and rate performance under low temperature conditions, and finally achieve the ultimate goal of low temperature commercialization. Although lots of efforts have been made in the field of low temperature performance, there are still a series of challenges to overcome. Based on the main points discussed in this paper, we propose several directions for the future development of low temperature electrolytes:

(1) Solid-liquid-solid conversion mechanism: determine the composition of the solvated junction and characterize the dynamic desolvation process.

Although advanced characterization methods and computational simulation have been developed to analyze the solvated structure of Li^+ , the specific parameters that determine the properties of the electrolyte are still unknown. Therefore, it is necessary to further explore the structural components of the solvated layer and the basic parameters (such as bond length, bond angle, etc.). Similarly, the desolvation process will also be unclear under low temperature conditions, and its dynamic process is related to the performance of the electrolyte. The improvement mechanism for lithium salts, solvents, and additives needs to be studied through advanced in-situ spectroscopy, quantum chemical calculations, etc. In addition, studies on the solvated layer of polysulfides reveal the electrolyte structure of polysulfides to explore a reasonable solution strategy.

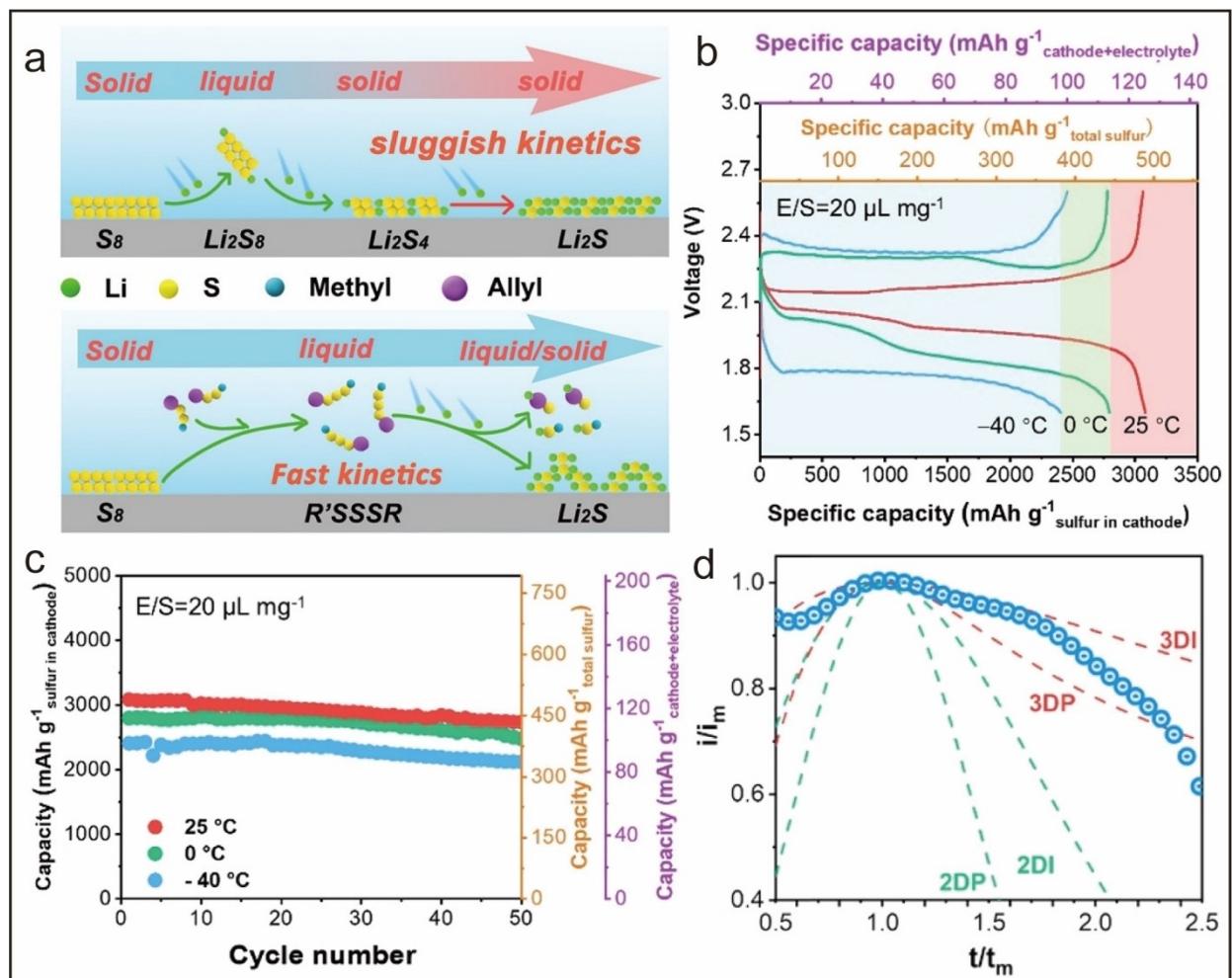


Figure 10. (a) Schematic illustration of the phase conversion in Li-S batteries in conventional electrolyte and AMDS-modified electrolyte. (b) Charge-discharge profiles and (c) Cycling performance of batteries using AMDS-modified at 25 °C, 0 °C and -40 °C. (d) Dimensionless transient at 2.08 V. Reproduced with permission.^[25] Copyright 2021, American Chemical Society.

(2) All-solid-phase conversion mechanism: the development of new fluoride electrolyte systems.

As we know, the all-solid-phase conversion process can ignore the polysulfide shuttle effect and a serious parasitic reaction. Today, the lithium anode realizes convenient kinetics through electrolyte chemistry at high voltage and ultralow temperature, mainly employing solvent fluorination. Although these fluorinated solvents or fluorinated anions can form a fluorine-rich SEI interface phase and improve the reversibility of metal anode, their high electronegativity will lead to other side reactions. Besides, the strong electron absorption behavior of fluorinated solvents will cause low dissolution of the lithium salt. Therefore, it is necessary to develop new fluorinated solvents with lower polar groups and nonsolvent cosolvents. What's more, choosing lithium salts with large anions ($-SO_2N$, $-(CF_2)_nCF_3$, $-SO_3^-$ and so on) with strong electron absorbing groups can further improve the stability of their fluorinated electrolyte system, making it possible to design and develop new low temperature electrolytes in the future.

(3) All-liquid-phase conversion mechanism: the application of new additives and an artificial SEI layer.

All-liquid-phase conversion is mainly used to convert the solid-solid conversion discharge platform into a fast liquid-phase reaction path, and its dynamic performance will be greatly improved. This mechanism can still play an excellent role in capacity storage under ultralow temperature conditions. Therefore, the development of other new additives can achieve liquid phase conversion of similar disulfides under low temperature conditions. However, this also poses a new challenge to the cycle stability of Li-S batteries. Serious shuttle effects and parasitic reactions can be alleviated by further constructing artificial SEI. Inorganic components in the SEI layer help to improve the low-temperature performance of lithium-metal batteries. Although the role of other organic components is not clear, their specific proportions need to be further studied.

Acknowledgements

This work was supported by National Natural Science Foundation of China, No. 52172250.

Conflict of Interests

The authors declare no competing financial interest.

Keywords: lithium-sulfur batteries · conversion mechanism · low temperature · electrolyte engineering

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Manuscript received: June 13, 2024

Revised manuscript received: July 13, 2024

Accepted manuscript online: July 15, 2024

Version of record online: September 6, 2024