

A perspective on energy chemistry of low-temperature lithium metal batteries

He Liu^{1,2}, Xinbing Cheng^{1,3} ✉, Chong Yan^{1,4}, Zeheng Li¹, Chenzi Zhao^{1,5}, Rong Xiang⁶, Hong Yuan⁷, Jiaqi Huang⁷ ✉, Elena Kuzmina⁸, Elena Karaseva⁸, Vladimir Kolosnitsyn⁸ and Qiang Zhang¹ ✉

ABSTRACT

Dendrite growth of lithium (Li) metal anode severely hinders its practical application, while the situation becomes more serious at low temperatures due to the sluggish kinetics of Li-ion diffusion. This perspective is intended to clearly understand the energy chemistry of low-temperature Li metal batteries (LMBs). The low-temperature chemistries between LMBs and traditional Li-ion batteries are firstly compared to figure out the features of the low-temperature LMBs. Li deposition behaviors at low temperatures are then discussed concerning the variation in Li-ion diffusion behaviors and solid electrolyte interphase (SEI) features. Subsequently, the strategies to enhance the diffusion kinetics of Li ions and suppress dendrite growth including designing electrolytes and electrode/electrolyte interfaces are analyzed. Finally, conclusions and outlooks are drawn to shed lights on the future design of high-performance low-temperature LMBs.

KEYWORDS

Lithium metal anode, lithium dendrite, low temperature, solid electrolyte interphase (SEI), ion-solvent complex, organic electrolyte.

Lithium (Li) metal anode has a theoretical specific capacity much higher than that of the traditional graphite anode (3860 vs. 372 mAh·g⁻¹) and the most negative electrode potential (-3.04 V vs. standard hydrogen electrode)^[1,2]. An extremely high energy density can be obtained when Li metal anode is adopted in working batteries. However, the toughest challenge during the practical application of Li metal batteries (LMBs) is Li dendrite growth^[3-5]. Strategies are proposed to suppress the dendrite growth of Li metal anodes, including regulating electrolyte and additive composition^[6-8], adopting solid-state electrolyte^[9-12], constructing specific solid electrolyte interphase (SEI)^[13-16], and designing host framework for Li metal anode^[17,18], etc. The validity of most strategies is verified at room temperature, boosting the Li utilization and lifespan of LMBs.

Batteries are required to operate at low temperatures (below 0 °C) in many practical working conditions^[19,20], such as electric vehicles, space exploration, subsea, and defense applications^[21-24]. The performance of LMBs is very sensitive to the working temperature since Li-ion diffusion and surface reactions are highly temperature-dependent processes. A noticeable drop in electrochemical performance of batteries can be observed below 0 °C, including specific capacity, rate capability, lifespan, duration of charging, safety, etc.^[25]. The poor performance of Li metal anodes operating at low temperatures can be mitigated by the addition of external or internal heating systems^[26]. However, this will inevitably

consume additional energy and increase the total system mass, consequently sacrificing the output energy efficiency and energy density of low-temperature batteries. Furthermore, heating strategy is easily confronted with safety issues caused by uneven heat transfer. Hence, more efforts are required to improve the battery chemistry via regulating the bulk and interfacial features. The prerequisite is a deep comprehension of low-temperature battery chemistries of LMBs.

Generally, the distribution and diffusion process of Li ions near the anode interface contribute mainly to the Li deposition behaviors in LMBs. Dendrite growth is a competition consequence between the Li-ion diffusion and surface reactions. Li-ion diffusion is a rate-determining step compared with the rapid reaction of Li ions on electrode surface^[27], resulting in a declined Li-ion concentration near the anode surface^[28]. At a specific point, dendrite growth initiates once the concentration of Li ions on electrode surface drops into zero^[29,30]. The desolvation and diffusion process of Li ions within the SEI contributes mainly to the impedance of Li-ion diffusion. This process becomes more sluggish at low temperatures, making dendrite issue more serious and complicated^[31,32].

It is undoubtedly that the cathode will affect the battery chemistry in the wide temperature range and in turn affect the cycling performance of the LMBs. On one hand, Li-ion diffusion at cathode side is a temperature-dependent process, including the

¹Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China; ²School of Chemistry and Materials Science, Nanjing University of Information Science & Technology, Nanjing 210044, China; ³Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 211189, China; ⁴Shanxi Research Institute for Clean Energy, Tsinghua University, Taiyuan 030032, China; ⁵State Key Laboratory of Automotive Safety and Energy, School of Vehicle and Mobility, Tsinghua University, Beijing 100084, China; ⁶Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan; ⁷Advanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, China; ⁸Ufa Institute of Chemistry UFRS RAS, Ufa 450054, Russia
Address correspondence to [Xinbing Cheng, chengxb@seu.edu.cn](mailto:Xinbing.Cheng@seu.edu.cn); [Jiaqi Huang, jqhuang@bit.edu.cn](mailto:Jiaqi.Huang@bit.edu.cn); [Qiang Zhang, zhang-qiang@mails.tsinghua.edu.cn](mailto:Qiang.Zhang, zhang-qiang@mails.tsinghua.edu.cn)

desolvation and diffusion of Li ions across the cathode interface, and the diffusion process inside the bulk cathode. This issue is fully investigated in Li-ion batteries with cathodes such as LiFePO_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM), LiCoO_2 , LiMn_2O_4 , etc.^[33,34] On the other hand, the cathode can also affect the Li deposition behaviors on anode side. Specifically, the cross talk between transition metal cathode and Li metal anode will affect the deposition/stripping behavior of Li dendrites^[35]. The dissolution and diffusion of polysulfides in Li-S batteries have considerable influence on the anode chemistry and cell performance. Temperature variation alters the dissolution and diffusion kinetics of transition metal cations and polysulfides, consequently contributing to the Li deposition behaviors. In addition, the compatibility of electrolytes toward high-voltage cathode and Li metal anode is nonnegligible when regulating electrolyte recipe for LMB full cells^[18]. However, this review focuses primarily on the low-temperature anode chemistry in LMBs. The detailed discussion on the cathode chemistry at low temperature is not covered considering that researches on this topic are mainly conducted in Li-ion batteries or room-temperature LMBs.

This perspective is intended to clearly understand the energy chemistry and emerging energy materials for low-temperature (below 0 °C) LMBs with focus on Li metal anodes. Firstly, the differences in low-temperature chemistries between LMBs and Li-ion batteries are compared to figure out the features of LMBs. Li deposition features at low temperature are then discussed. Later, the strategies in suppressing dendrite growth including designing electrolytes and electrode/electrolyte interfaces are explored. Finally, conclusions and outlooks are drawn to shed lights on the future design of high-performance LMBs at low temperatures.

1 Chemical features of low-temperature LMBs

Compared with the traditional Li-ion batteries, LMBs present several differences in low-temperature battery chemistries. (1) Solvents for low-temperature operation. In Li-ion batteries, ethylene carbonate (EC) is nearly an indispensable electrolyte component to construct a favorable SEI on a graphite surface^[36]. However, EC possesses a high freezing point of 39 °C, resulting in an inferior ionic conductivity at low temperatures. A strong coordination between EC and Li ions also leads to an intrinsically high desolvation energy barrier before Li ions intercalating into graphite interlayers^[37,38]. Instead, LMBs can be operated in an EC-free electrolyte, providing more chances for selecting solvents with low freezing point and superior desolvation kinetics. Specifically, the primary solvents in lithium-sulfur (Li-S) batteries are dioxolane (DOL) and dimethoxyethane (DME). Both of them exhibit very low freezing points of -95 and -58 °C, respectively, offering a high ionic conductivity of $0.4 \text{ mS}\cdot\text{cm}^{-1}$ even at -80 °C^[39-43].

(2) Interfacial features at low temperatures. The SEI in Li-ion batteries is relatively stable due to the insertion mechanism of graphite anodes compared with the conversion mechanism in Li metal anodes. Nonetheless, the SEI on graphite surface tends to be unstable as temperature goes down since metallic Li starts to plate on anode. In contrast, some unexpected phenomena are observed in Li metal anodes. The SEI on Li metal anodes is chemically and structurally distinct, and contains much more inorganic components at low temperatures, such as LiF and Li_2CO_3 ^[40,41]. These species are significant in terms of stabilizing SEI layer, considering their superior electronic insulation, high chemical stability against organic electrolytes, and high mechanical modulus^[44-47]. The interfaces between LiF particles can be important channels to transfer

Li ions and enhance the ionic conductivity in the LiF-based SEI^[48]. In addition, the formed SEI is found to be thinner resulting from the lower reaction rates^[49,50]. Synergistically, the thinner and less resistive SEI layers at low temperatures may lead to a reduced charge transfer resistance through SEI^[40,51]. This is critically important as the charge transfer resistance through SEI could be one of the limiting steps in determining the low-temperature performance.

(3) Diffusion process inside the bulk anodes. In Li metal anode, Li ions directly accept electrons on electrode surface and turn into Li metal once they travel through the SEI layer. However, desolvated Li ions across the SEI need to further diffuse inside the graphite interlayer before they intercalate into the anode to form Li_xC_6 compound in graphite anode^[25,52,53]. This additional step generates more diffusion barrier for Li ions, aggravating the complexity of diffusion process at low temperatures.

With more choices in electrolyte components, thinner and less resistive SEI layers formed at low temperatures, and reduced diffusion process inside the bulk anodes, LMBs may potentially be more suitable for critical low-temperature applications with high performance and high energy density, compared with the counterparts of Li-ion batteries. However, the aggregated dendrite growth and deteriorated electrochemical performance at low temperatures must be handled before the practical applications. It is quite challenging to conquer these issues and realize low-temperature application of LMBs.

2 Li deposition behaviors at low temperatures

Dendrite growth is aggravated with limited kinetics of Li-ion transfer based on Sand's time model. The restricted Li-ion diffusion process at low temperatures leads to obviously different Li deposition behaviors, which severely impedes the electrochemical performance of Li metal anodes (see Figure 1)^[49,54]. Firstly, Li deposition morphology varies considerably as temperature goes down. Smaller nucleation size and uneven Li-ion distribution at low temperatures lead to Li deposition with a higher specific surface area, resulting in more side reactions with electrolytes and declined Li utilization^[28,31]. At a low temperature of 170 K, the growth speed of Li cluster is much slowed down by several orders of magnitude relative to that of room temperature^[55]. Secondly, largely increased impedance and polarization are frequently observed at low temperatures, contributing to only 30%–50% lifespan retention of LMBs working at room temperature. Hence, low working temperature generates significant impacts on the Li utilization and lifespan of Li metal anodes.

Revealing the dendrite growth mechanism is prerequisite to improve the electrochemical performance of Li metal anodes at low temperatures. This requires detailed analysis of potential effects that temperature could generate on every step of Li plating process (Figure 2). Li ion from cathode undergoes the following process successively before it gets electrons and turns into Li metal at anode surface^[56-60]: Li ion travels across the cathode interface, enters the bulk electrolyte, and gets solvated with anions or solvents. Then the solvated Li ion diffuses through the electrolyte before it enters SEI film on anode surface. Finally, it gets desolvated and moves across the SEI film, followed by reacting with electrons and transforming into Li. Notably, the mechanical properties of SEI film also influence the distribution of Li ion flux on Li anode surface, which determines the growth direction of Li metal^[61,62]. Here comes the question: which is the rate-determining step causing Li dendrite growth at low temperatures? Theoretic-

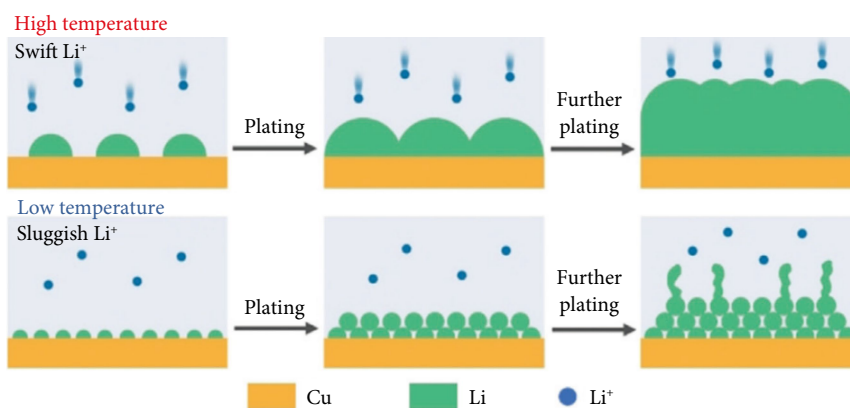


Fig. 1 Comparison of Li deposition behavior at different temperatures, indicating aggravated dendrite growth at low temperatures due to the sluggish diffusion kinetics of Li ions (reprinted with permission from Ref. [49], © 2019 Wiley).

ally, every step in this process is temperature-dependent. Considering the reaction between Li ion and electrons, and electron transfer process are ultra-fast, the limiting factor is focused on the diffusion process of Li ions and mechanical properties of SEI films^[50]. The charge transfer resistance is primarily contributed by the desolvation of Li ions at the interface and Li ions travelling across the SEI film^[38]. However, the highly active and unstable interface in Li metal anodes makes it hard to determine the specific

limiting step in LMBs. The various interfacial chemistries make the process more complicated at low temperatures. More advanced in-situ characterization techniques are urgently requested to exploit the interfacial properties of Li metal anodes and figure out the limiting step at various temperatures. Notably, the feature of SEI film is crucial to determine the interfacial process. SEI film with a high mechanical modulus can restrain the dendrite growth^[63,64].

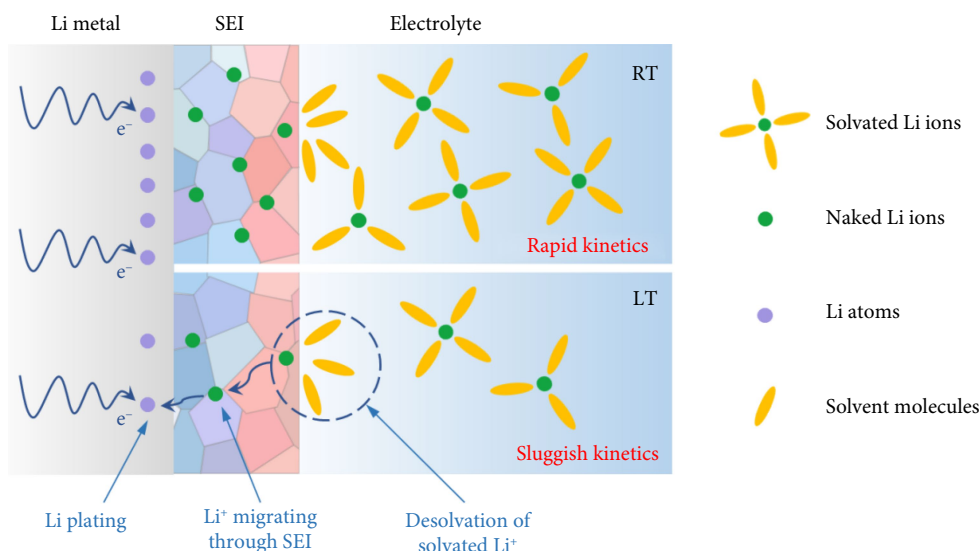


Fig. 2 Schematic diagram illustrating the diffusion process of Li ions from cathode to anode surface followed by reacting with electrons and transforming into Li metal.

The decrease in temperature will directly affect the solvation structure of Li ions and the properties of SEI, thereby affecting the growth behavior of dendrites^[30,65]. It is generally believed that low temperature will increase the diffusion impedance of Li ions. Low temperature will also slow down the reaction kinetics between Li metal anode and electrolyte, thus generating a thinner SEI even with an increased ion conductivity in some specific electrolyte system^[40,41]. In addition, another significant change is the increasing percentage of inorganic components in SEI with decreasing temperatures^[41], rendering a higher mechanical modulus of SEI film. Theoretically, this film should be capable of well inhibiting the growth of dendrites^[66]. However, the uncertain influence of temperature on the Li-ion solvation structure and SEI properties exacerbates the complexity to unveil the dendrite growth mechanism

at low temperatures.

More elaborate and targeted strategies are required to address the aggravated dendrite growth issues at low temperatures based on the low-temperature battery chemistry. The key of inhibiting dendrite growth at low temperature is to enhance the ionic conductivity and build a stable SEI at the interface, which can prevent the side reactions between the electrolyte and Li metal during the long cycles. The smaller size and higher specific surface area of metallic Li dendrites at low temperatures inevitably render increased side reactions and low Li utilization of Li metal anodes. Furthermore, the extremely high strength of micrometer-sized Li at low temperatures makes it more difficult to suppress its dendrite growth^[67]. In addition, simply employing electrolytes with high bulk ionic conductivity is insufficient to satisfy the low-temperature

ure battery system, since the desolvation and transport of Li ions through the interfaces contribute a lot to the Li-ion diffusion resistance. All these challenges put forward higher demands in the mechanical, conductive properties, and long-term stability of SEI films^[68], as well as the solvation structures of Li ions in the solvents^[69]. This requires meticulously design of electrolyte recipes and electrode structures with comprehensively considering the above effects in order to achieve good electrochemical performance at low temperatures.

3 Strategies in boosting low-temperature performance

3.1 Electrolyte design

Intuitively, the foremost strategy in boosting low-temperature performance of LMBs is tailoring the ingredient of electrolytes, which is facile to realize. Subtly designing electrolytes can not only enhance the bulk ionic conductivity in a wide operating temperature range, but also provide opportunities to achieve an optim-

ized solvation structure of Li ions with low desolvation barriers. In addition, the SEI features are also highly dependent on the electrolyte components. Therefore, most of the published works in boosting the low-temperature performances of LMBs focus on regulating the constituent of electrolytes to render a high bulk ionic conductivity, optimized solvation structure, and robust SEI at working temperatures (Figure 3)^[21].

The bulk ionic conductivity of electrolytes needs to be concerned when selecting appropriate electrolytes for LMBs at low temperatures. Ensuring a high ionic conductivity of electrolytes at low temperatures is the prerequisite to acquire LMBs which can be efficiently operated at low temperatures. This rule is not quite important for designing room-temperature electrolytes since most of the non-aqueous electrolytes offer high ionic conductivity at room temperature. However, the viscosity of the electrolyte largely increases with the decreased temperatures, leading to a low ionic conductivity. Optimizing the components and ratios of the solvents is the frequently adopted strategy to reduce the freezing-point and improve the ionic conductivity of electrolytes at low temperatures^[70,71].

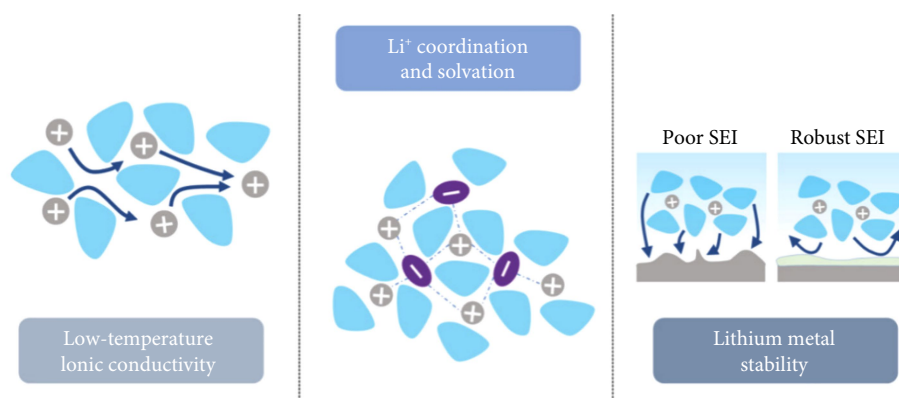


Fig. 3 The role of electrolyte design on the low-temperature chemistry of Li metal anodes including regulating the ionic conductivity of electrolyte, the solvation structure of Li ions, and the properties of SEI films (reprinted with permission from Ref. [21], © 2020 Wiley).

Solvents with a low melting point are extensively adopted in low-temperature LMBs^[72], such as ethyl acetate with a freezing-point of -84 °C. Dichloromethane with a low melting point of -95 °C is usually adopted as a diluent of highly concentrated electrolytes, which has been demonstrated to be an effective co-solvent in protecting Li metal anodes at even -70 °C^[73]. Designing electrolytes with a high ionic conductivity usually requires solvents possessing a high dielectric constant to efficiently dissociate Li ions from the anions and achieve a high Li-ion concentration in the electrolyte. However, the high dielectric constant of solvents induces strong binding between Li ions and the solvent molecules, consequently leading to a large desolvation barrier of Li ions at the interfaces and reduced Li-ion transference number in electrolyte. The high dielectric constant also strengthens the dipole–dipole force within the highly polar molecules, resulting in an elevated freezing temperature of electrolytes. All these effects may deteriorate the low-temperature performance of working batteries^[74]. The recipe meeting both features varies depending on the temperatures. Hence, it is challenging to design non-aqueous electrolytes with high ionic conductivity in a wide temperature range.

As mentioned above, only regulating the bulk ionic conductivity of electrolytes is far from adequate to achieve a high-performance low-temperature battery. The solvation structures of Li ions and SEI features also need to be considered since the desolvation

and transport of Li ions through the interfaces could be the rate-limiting steps. A poorly solvating solvent is preferred to acquire a weak coordination between Li ions and surrounding solvent molecules or anions, thus ensuring a relatively low desolvation energy and charge transfer resistance^[75]. Recently, Holoubek et al. confirmed that the local solvation structure of Li ions dictates the low-temperature performance of LMBs by comparing diethyl ether (DEE) with DOL/DME control electrolyte after excluding the contribution of ionic conductivity and SEI compositions^[69]. A much lower binding energy between Li ions and DEE (-280 kJ·mol⁻¹) relative to that of DOL/DME system (-414 kJ·mol⁻¹) renders uniform Li deposition behavior and a high Coulombic efficiency of 98.4% at even -60 °C.

To handle the issues of the strong coordination between solvents and Li ions, Fan et al. constructed a super-electrolyte with a high ionic conductivity by dissolving the all-fluorinated electrolytes into the highly fluorinated non-polar solvents (Figure 4(a))^[74]. In the electrolyte, the affinity between Li ions and the non-polar solvents is much weaker than that of Li ions and fluorinated carbonates. The non-polar solvents can effectively break the strong binding between the highly polar molecules, which can efficiently increase the Li-ion transference number. The weakly-solvating electrolyte can also affect the components of SEI (Figure 5)^[76]. As the solvation ability of Li ions decreases, the anion content in the

solvated inner layer increases, and the interface chemistry exhibit a transition from a solvent-dominated to anion-dominated process. The anion-induced SEI is a homogeneous structure dominated by inorganic products with a significantly reduced Li-ion diffusion barrier. This can effectively increase the diffusion kinetics at low temperatures.

The electrolyte researches for Li batteries mostly focus on liquid-based systems because of the relatively high ionic conductivity at room temperature. However, the high melting point leads to decreased ionic conductivities at low temperatures. Recently, the fluoromethane (CH_3F)-based liquefied gas electrolytes presented a superior electrochemical performance even down to -60°C (Fig-

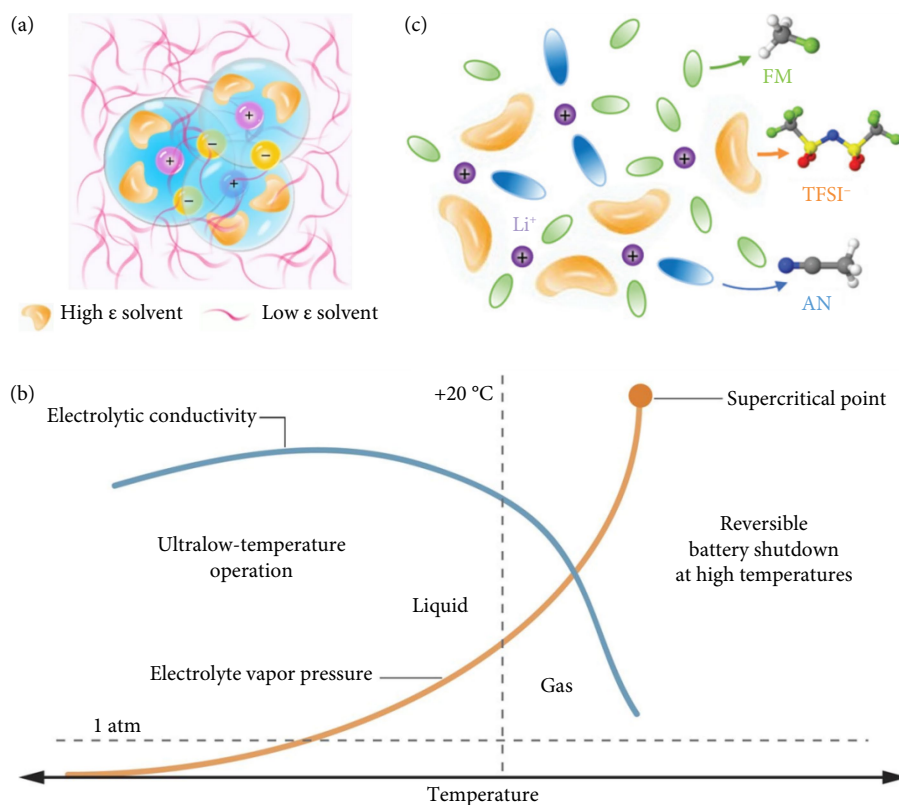


Fig. 4 Designing electrolytes with optimized solvation structure to render a low desolvation barrier and high ionic conductivity at low temperatures. (a) The interactions between Li ions and solvents in fluorinated electrolytes with non-polar solvents (reprinted with permission from Ref. [74], © The Author(s), under exclusive licence to Springer Nature Limited 2019). (b) Variation of electrolytic conductivity and pressure with temperature of liquefied gas electrolytes (reprinted with permission from Ref. [76], © 2017 The American Association for the Advancement of Science). (c) The solvation structure of liquefied gas electrolytes (reprinted with permission from Ref. [77], © The Royal Society of Chemistry 2020).

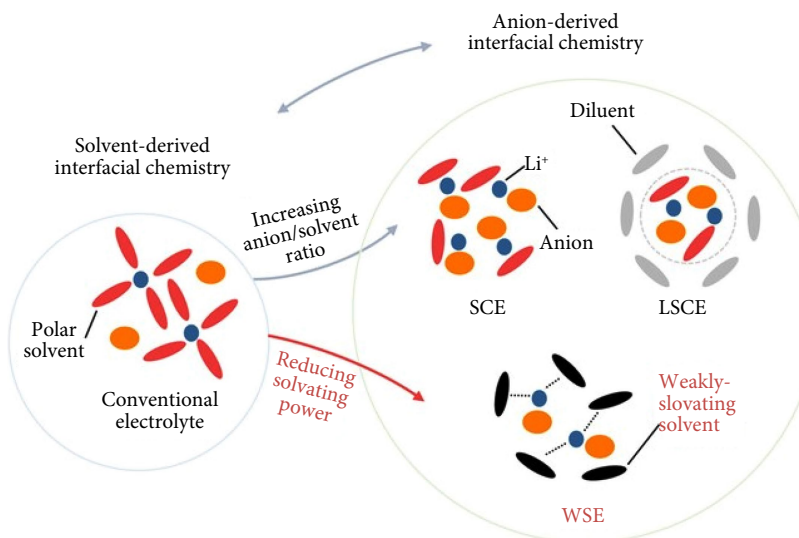


Fig. 5 The solvation structures of Li ions and corresponding interfacial chemistry in various electrolytes. SCE: superconcentrated electrolyte, LSCE: localized superconcentrated electrolyte, WSE: weakly solvating electrolyte (reprinted with permission from Ref. [78], © 2020 Wiley).

ure 4(b))^[76]. The high ionic conductivity at low temperatures is originated from the low boiling/melting point and low viscosity of liquefied gas electrolytes. The salt solubility and ionic conductivity are further elevated by introducing tetrahydrofuran (THF) as a cosolvent, which facilitates high desolvation kinetics (Figure 4(c))^[77]. However, such a superior performance at low temperatures is obtained by sacrificing safety at room temperature, because the batteries with liquid gas have to be protected with extremely sophisticated equipment to maintain the high pressure of tens of bars.

The most significant change with the decreasing temperatures lies in the kinetics of Li-ion diffusion^[79,80]. In this regard, regulating electrolyte components to achieve a high ionic conductivity at low temperatures is a facile solution^[81–84]. The interaction between Li ions and solvents/anions also needs to be considered to realize a rapid desolvation and diffusion process at the interfaces. This concept is also suitable for designing electrolytes for all the batteries operating at low temperatures besides LMBs. In addition, the compatibility of electrolytes toward high-voltage cathode and Li metal anode needs to be concerned to construct stable cathode/anode interfaces simultaneously in LMB full cells.

3.2 SEI design

Besides the retarded diffusion kinetics in the electrolyte, the operating temperature also has obvious effects on the structure and chemistry of SEI. It was found that in conventional carbonate ester electrolytes, the $-15\text{ }^{\circ}\text{C}$ operation renders the SEI highly crystalline and inhomogeneous with Li_2CO_3 -dominant structure^[85], while in ether electrolyte, the $-40\text{ }^{\circ}\text{C}$ operation leads to a SEI layer with more highly-crystalline LiF and less polymer species (Figure 6(a))^[41]. The distribution of SEI components in depth and across the entire surface also differs with the varying temperatures^[86]. The structure, components, thickness, and ionic conductivity of SEI film are largely altered as the temperature goes down, which determines the nucleation and deposition behaviors of Li metal anodes^[41,49].

The sluggish diffusion kinetics of Li ions across the SEI results in rapid depletion of Li ions at the interface, triggering early initiation of Li dendrites at low temperatures (Figure 6(b))^[87]. Improving the ionic conductivity of SEI is critically important for the efficient operation of low-temperature Li metal anodes. Xiao et al. regulated the interfacial chemistry by introducing a multifunctional high-donor-number solvent, tris(pyrrrolidinophosphine) oxide (TPPO) into carbonate electrolyte^[88]. LiNO_3 is easily dissolved caused by the strong binding between TPPO and Li ions, forming a Li_3N -rich SEI with high ionic conductivities. This robust SEI enables stable operation of LMBs in the temperature ranging from -15 to $70\text{ }^{\circ}\text{C}$. An all-fluorinated ester electrolyte was constructed to form a fluorine-rich SEI, which provides high capacities of 161, 149, and $133\text{ mAh}\cdot\text{g}^{-1}$ of $\text{Li}||\text{NCM811}$ cell operating at -40 , -50 , and $-60\text{ }^{\circ}\text{C}$ ^[89].

The SEI components can be facily tailored through the employment of different solvents and Li salts^[89]. However, the uncertainty and complexity of SEI properties varying with the temperatures make it tough to precisely control the SEI chemistry by simply regulating electrolytes. In this case, ex-situ artificial SEI is an alternative strategy to boost the ionic conductivity of SEI^[90]. Gao et al. constructed self-assembled monolayer of 1,3-benzene-disulfonyl fluoride (EAM) as an artificial SEI film to stabilize Li metal anodes at low temperatures^[85]. This artificial SEI layer can regulate the interfacial components by forming amorphous LiF nuclei, which can increase the ionic conductivity and guide uni-

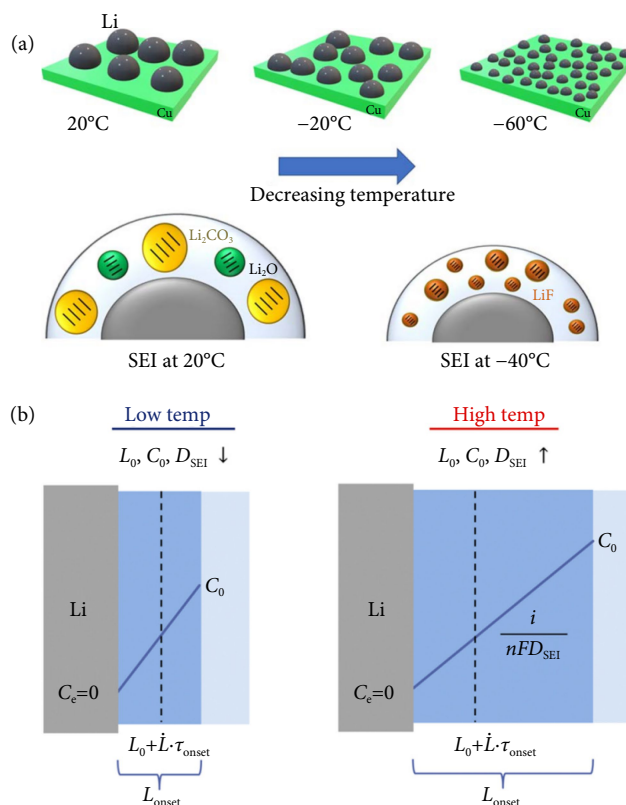


Fig. 6 Temperature dependence of SEI features as well as their impacts on the Li diffusion kinetics within SEI and Li deposition behaviors. (a) The structure and chemistry of SEI formed at 20 and $-40\text{ }^{\circ}\text{C}$ in an ether-based electrolyte and their corresponding Li deposition behaviors (reprinted with permission from Ref. [41], © 2019 American Chemical Society). (b) The effect of temperature on the variation of SEI thickness and initiation of Li dendrites (reprinted with permission from Ref. [87], © 2020 The Author(s)).

form Li nucleation^[78,91,92]. The multilayered artificial SEI with a LiF-rich inner phase and an amorphous outer layer renders stable Li deposition behavior at a low temperature even to $-60\text{ }^{\circ}\text{C}$ (Figure 7).

SEI film on Li metal anode is critically important in determining Li deposition behaviors^[82,93–96]. The structure and chemistry of SEI affect Li-ion transport properties, further acting on the nucleation and deposition of Li metal^[97–99]. The mechanical features of SEI also have effects on the growth tendency of Li dendrites^[100–103]. Noteworthy, most of the published works on SEI regulation at low temperatures mainly focus on its conductive properties, while more attentions are necessary to figure out the relationships with Li dendrites.

4 Conclusion and outlook

At present, the researches on the dendritic growth behavior of low-temperature Li metal anodes are still in the infancy, and the effects of temperature variation on the ionic diffusion features and interfacial properties of Li metal anodes are not yet clear. More severe dendrite growth at low temperatures happens compared with Li metal anode operating at room temperature. It is necessary to deeply understand the low-temperature battery chemistry in order to inhibit the dendrite growth and achieve LMBs with high specific energy density and long lifespan at low temperatures.

Electrolyte and SEI design are predominantly conducted to enhance the Li-ion diffusion kinetics and suppress dendrite growth.

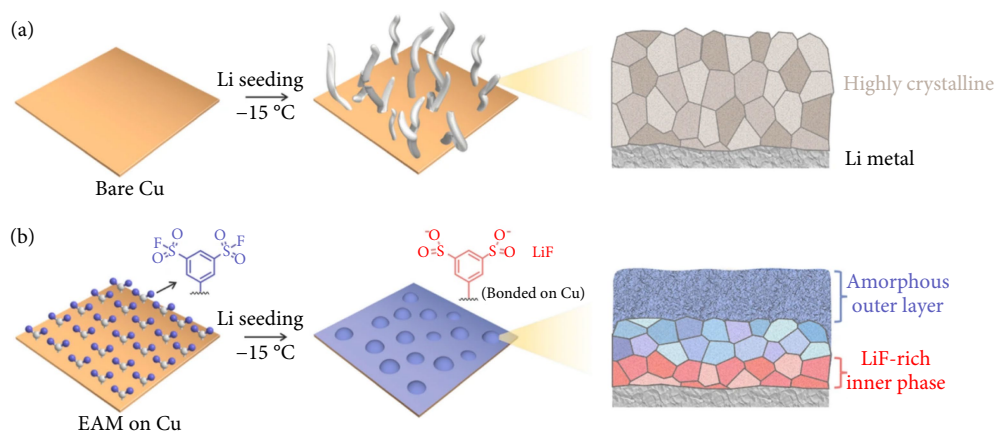


Fig. 7 A multilayered artificial SEI formed on the Cu substrate with EAM regulated structure and chemistry (reprinted with permission from Ref. [85], © The Author(s), under exclusive licence to Springer Nature Limited 2020).

Most of the previous researches focus on handling the issues of impeded kinetics at low temperatures similar with that in Li-ion batteries. Specifically, the weakly-solvated electrolyte is designed to improve the ionic conductivity of electrolytes and facilitate the desolvation process at the interfaces. SEI with more inorganic constituents and Li-ion diffusion channels is designed to improve its ionic conductivity.

Notably, stable and uniform Li deposition behaviors during the long-term cycling cannot be guaranteed with only the enhanced diffusion of Li ions. SEI with high modulus and high elasticity is also necessary to sustain the long-term stability of interfaces and suppress dendrite growth during the whole service time of working LMBs. In this respect, host framework design is also an indispensable solution, since the skeleton provides space for Li deposition, thus mitigating the volume fluctuation of electrodes and facilitating the stability of SEI during repeated charge/discharge process. Furthermore, the lithiophilicity and conductivity of the host can be tuned to offer ideal diffusion kinetics and uniform Li ion flux on electrode surface at low temperatures^[104]. Some other strategies in restricting dendrite growth at room temperature are also potential choices in regulating the low-temperature electrochemical processes, such as employing Li alloy anode with a high ionic conductivity^[105–107], altering charge protocol to alleviate the Li-ion depletion on electrode surface^[108,109], etc. The performance of low-temperature LMBs will be remarkably improved through the synergy of multiple strategies.

Although challenges remain for the practical applications of LMBs even at room temperature due to the poor lifespan, it is still imperative to get insight into the low-temperature battery chemistry of LMBs. On one hand, the feasibility of room-temperature strategies in protecting Li metal anodes at low temperature is a mystery considering the unique battery chemistry depending on the temperatures. On the other hand, the investigation on the low-temperature battery chemistry in LMBs can also provide guidance for developing high-performance room-temperature LMBs and addressing dendrite plating issues of Li-ion batteries at low temperatures. The most pressing issue in exploiting low-temperature LMBs is to reveal the interfacial chemistry and its evolution process with the varying temperatures considering the intrinsically limiting kinetics at electrode/electrolyte interfaces^[86,100]. Therefore, exploiting advanced characterization techniques is imperative to uncover the interfacial features at different temperatures and unveil the mechanisms of aggravated dendrite growth at low temperatures. This facilitates a rational and targeted design of energy chemistry and materials in LMBs to achieve superior low-temper-

ature electrochemical performances. Ultimately, high-energy-density LMBs with a wide operation temperature range can meet the demands in many performance-critical applications.

Acknowledgements

This work was supported by National Natural Science Foundation of China (22179070, 22109083, 22108151, 22075029, and 22061132002), China Postdoctoral Science Foundation (BX2021135, 2021TQ0164), the Seed Fund of Shanxi Research Institute for Clean Energy (SXYJF015), the Tsinghua University Initiative Scientific Research Program, and the “Shuimu Tsinghua Scholar Program of Tsinghua University”.

Article history

Received: 24 December 2021; Revised: 2 February 2022; Accepted: 21 February 2022

Additional information

© 2022 The Author(s). This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

References

- Wang, Y. Y., Wang, Z. J., Zhao, L., Fan, Q. N., Zeng, X. H., Liu, S. L., Pang, W. K., He, Y. B., Guo, Z. P. (2021). Lithium metal electrode with increased air stability and robust solid electrolyte interphase realized by silane coupling agent modification. *Advanced Materials*, 33: 2008133.
- Liu, H., Cheng, X. B., Xu, R., Zhang, X. Q., Yan, C., Huang, J. Q., Zhang, Q. (2019). Plating/stripping behavior of actual lithium metal anode. *Advanced Energy Materials*, 9: 1902254.
- Chen, X. R., Zhao, B. C., Yan, C., Zhang, Q. (2021). Review on Li deposition in working batteries: From nucleation to early growth. *Advanced Materials*, 33: 2004128.
- Wu, J. Y., Rao, Z. X., Liu, X. T., Shen, Y., Fang, C., Yuan, L. X., Li, Z., Zhang, W. X., Xie, X. L., Huang, Y. H. (2021). Polycationic polymer layer for air-stable and dendrite-free Li metal anodes in carbonate electrolytes. *Advanced Materials*, 33: 2007428.
- Lin, X. D., Gu, Y., Shen, X. R., Wang, W. W., Hong, Y. H., Wu,

- Q. H., Zhou, Z. Y., Wu, D. Y., Chang, J. K., Zheng, M. S., et al. (2021). Correction: An oxygen-blocking oriented multifunctional solid–electrolyte interphase as a protective layer for a lithium metal anode in lithium–oxygen batteries. *Energy & Environmental Science*, 14: 1439–1448.
- [6] Qian, K., Liu, Y. Z., Zhou, X. W., Gosztola, D. J., Nguyen, H., Li, T. (2021). Decoupling the degradation factors of Ni-rich NMC/Li metal batteries using concentrated electrolytes. *Energy Storage Materials*, 41: 222–229.
- [7] Wang, H. P., He, J., Liu, J. D., Qi, S. H., Wu, M. G., Wen, J., Chen, Y. N., Feng, Y. Z., Ma, J. M. (2021). Electrolytes enriched by crown ethers for lithium metal batteries. *Advanced Functional Materials*, 31: 2002578.
- [8] Liu, J., Yuan, H., Tao, X. Y., Liang, Y. R., Yang, S. J., Huang, J. Q., Yuan, T. Q., Titirici, M. M., Zhang, Q. (2020). Recent progress on biomass-derived ecomaterials toward advanced rechargeable lithium batteries. *EcoMat*, 2: e12019.
- [9] Chen, W. P., Duan, H., Shi, J. L., Qian, Y. M., Wan, J., Zhang, X. D., Sheng, H., Guan, B., Wen, R., Yin, Y. X., et al. (2021). Bridging interparticle Li⁺ conduction in a soft ceramic oxide electrolyte. *Journal of the American Chemical Society*, 143: 5717–5726.
- [10] Shen, L. D., Liu, X., Dong, J., Zhang, Y. T., Xu, C. X., Lai, C., Zhang, S. Q. (2021). Functional lithiophilic polymer modified separator for dendrite-free and pulverization-free lithium metal batteries. *Journal of Energy Chemistry*, 52: 262–268.
- [11] Liu, H., Cheng, X. B., Huang, J. Q., Yuan, H., Lu, Y., Yan, C., Zhu, G. L., Xu, R., Zhao, C. Z., Hou, L. P., et al. (2020). Controlling dendrite growth in solid-state electrolytes. *ACS Energy Letters*, 5: 833–843.
- [12] Wu, X. X., Zheng, Y. J., Li, W. B., Liu, Y. Y., Zhang, Y., Li, Y. J., Li, C. L. (2021). Solid electrolytes reinforced by infinite coordination polymer nano-network for dendrite-free lithium metal batteries. *Energy Storage Materials*, 41: 436–447.
- [13] Xu, X. Q., Xu, R., Cheng, X. B., Xiao, Y., Peng, H. J., Yuan, H., Liu, F. Y. (2021). A two-dimension laminar composite protective layer for dendrite-free lithium metal anode. *Journal of Energy Chemistry*, 56: 391–394.
- [14] Yang, S. J., Yao, N., Xu, X. Q., Jiang, F. N., Chen, X., Liu, H., Yuan, H., Huang, J. Q., Cheng, X. B. (2021). Formation mechanism of the solid electrolyte interphase in different ester electrolytes. *Journal of Materials Chemistry A*, 9: 19664–19668.
- [15] Li, F., He, J., Liu, J. D., Wu, M. G., Hou, Y. Y., Wang, H. P., Qi, S. H., Liu, Q. H., Hu, J. W., Ma, J. M. (2021). Gradient solid electrolyte interphase and lithium-ion solvation regulated by bisfluoroacetamide for stable lithium metal batteries. *Angewandte Chemie International Edition*, 60: 6600–6608.
- [16] Huo, H., Gao, J., Zhao, N., Zhang, D., Holmes, N. G., Li, X., Sun, Y., Fu, J., Li, R., Guo, X., et al. (2021). A flexible electron-blocking interfacial shield for dendrite-free solid lithium metal batteries. *Nature Communications*, 12: 176.
- [17] Liu, H., Cheng, X. B., Zhang, R., Shi, P., Shen, X., Chen, X. R., Li, T., Huang, J. Q., Zhang, Q. (2020). Mesoporous graphene hosts for dendrite-free lithium metal anode in working rechargeable batteries. *Transactions of Tianjin University*, 26: 127–134.
- [18] Liu, H., Li, T., Xu, X. Q., Shi, P., Zhang, X. Q., Xu, R., Cheng, X. B., Huang, J. Q. (2021). Stable interfaces constructed by concentrated ether electrolytes to render robust lithium metal batteries. *Chinese Journal of Chemical Engineering*, 37: 152–158.
- [19] Zhu, G. L., Wen, K. C., Lv, W. Q., Zhou, X. Z., Liang, Y. C., Yang, F., Chen, Z. L., Zou, M. D., Li, J. C., Zhang, Y. Q., et al. (2015). Materials insights into low-temperature performances of lithium-ion batteries. *Journal of Power Sources*, 300: 29–40.
- [20] Zhao, C. X., Liu, J. N., Yao, N., Wang, J., Ren, D., Chen, X., Li, B. Q., Zhang, Q. (2021). Can aqueous zinc–air batteries work at sub-zero temperatures. *Angewandte Chemie International Edition*, 60: 15281–15285.
- [21] Gupta, A., Manthiram, A. (2020). Designing advanced lithium-based batteries for low-temperature conditions. *Advanced Energy Materials*, 10: 2001972.
- [22] Liang, Y. R., Zhao, C. Z., Yuan, H., Chen, Y., Zhang, W. C., Huang, J. Q., Yu, D. S., Liu, Y. L., Titirici, M. M., Chueh, Y. L., et al. (2019). A review of rechargeable batteries for portable electronic devices. *InfoMat*, 1: 6–32.
- [23] Kong, L., Tang, C., Peng, H. J., Huang, J. Q., Zhang, Q. (2020). Advanced energy materials for flexible batteries in energy storage: A review. *SmartMat*, 1: e1007.
- [24] Cheng, X. B., Liu, H., Yuan, H., Peng, H. J., Tang, C., Huang, J. Q., Zhang, Q. (2021). A perspective on sustainable energy materials for lithium batteries. *SusMat*, 1: 38–50.
- [25] Dong, X. L., Wang, Y. G., Xia, Y. Y. (2021). Promoting rechargeable batteries operated at low temperature. *Accounts of Chemical Research*, 54: 3883–3894.
- [26] Wang, C. Y., Zhang, G., Ge, S., Xu, T., Ji, Y., Yang, X. G., Leng, Y. (2016). Lithium-ion battery structure that self-heats at low temperatures. *Nature*, 529: 515–518.
- [27] Xu, X. Y., Liu, Y. Y., Hwang, J. Y., Kapitanova, O. O., Song, Z. X., Sun, Y. K., Matic, A., Xiong, S. Z. (2020). Role of Li-ion depletion on electrode surface: underlying mechanism for electrodeposition behavior of lithium metal anode. *Advanced Energy Materials*, 10: 2002390.
- [28] Han, Y. H., Jie, Y. L., Huang, F. Y., Chen, Y. W., Lei, Z. W., Zhang, G. Q., Ren, X. D., Qin, L. J., Cao, R. G., Jiao, S. H. (2019). Enabling stable lithium metal anode through electrochemical kinetics manipulation. *Advanced Functional Materials*, 29: 1904629.
- [29] Zhu, F. L., Bao, H. F., Wu, X. S., Tao, Y. L., Qin, C., Su, Z. M., Kang, Z. H. (2019). High-performance metal-organic framework-based single ion conducting solid-state electrolytes for low-temperature lithium metal batteries. *ACS Applied Materials & Interfaces*, 11: 43206–43213.
- [30] Liu, H., Cheng, X. B., Jin, Z. H., Zhang, R., Wang, G. X., Chen, L. Q., Liu, Q. B., Huang, J. Q., Zhang, Q. (2019). Recent advances in understanding dendrite growth on alkali metal anodes. *Energy-Chem*, 1: 100003.
- [31] Love, C. T., Baturina, O. A., Swider-Lyons, K. E. (2015). Observation of lithium dendrites at ambient temperature and below. *ECS Electrochemistry Letters*, 4: A24–A27.
- [32] Zhao, Q., Liu, X., Zheng, J. X., Deng, Y., Warren, A., Zhang, Q. Y., Archer, L. (2020). Designing electrolytes with polymerlike glass-forming properties and fast ion transport at low temperatures. *Proceedings of the National Academy of Sciences of the United States of America*, 117: 26053–26060.
- [33] Cui, S. H., Wei, Y., Liu, T. C., Deng, W. J., Hu, Z. X., Su, Y. T., Li, H., Li, M. F., Guo, H., Duan, Y. D., et al. (2016). Optimized temperature effect of Li-ion diffusion with layer distance in Li(Ni_{0.8}M_{0.2})Co₂O₂ cathode materials for high performance Li-ion battery. *Advanced Energy Materials*, 6: 1501309.
- [34] Tang, Z. F., Wang, S., Liao, J. Y., Wang, S., He, X. D., Pan, B. C., He, H. Y., Chen, C. H. (2019). Facilitating lithium-ion diffusion in layered cathode materials by introducing Li⁺/Ni²⁺ antisite defects for high-rate Li-ion batteries. *Research*, 2019: 2198906.
- [35] Betz, J., Brinkmann, J. P., Nölle, R., Lürenbaum, C., Kolek, M., Stan, M. C., Winter, M., Placke, T. (2019). Cross talk between transition metal cathode and Li metal anode: unraveling its influence on the deposition/dissolution behavior and morphology of lithium. *Advanced Energy Materials*, 9: 1900574.
- [36] Xu, K. (2004). Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chemical Reviews*, 104: 4303–4418.
- [37] Xu, K., Lam, Y., Zhang, S. S., Jow, T. R., Curtis, T. B. (2007). Solvation sheath of Li⁺ in nonaqueous electrolytes and its implication of graphite/electrolyte interface chemistry. *The Journal of Physical Chemistry C*, 111: 7411–7421.
- [38] Li, Q. Y., Lu, D. P., Zheng, J. M., Jiao, S. H., Luo, L. L., Wang, C. M., Xu, K., Zhang, J. G., Xu, W. (2017). Li⁺-desolvation dictating lithium-ion battery's low-temperature performances. *ACS Applied Materials & Interfaces*, 9: 42761–42768.
- [39] Gupta, A., Bhargava, A., Jones, J. P., Bugga, R. V., Manthiram, A. (2020). Influence of lithium polysulfide clustering on the kinetics

- of electrochemical conversion in lithium-sulfur batteries. *Chemistry of Materials: A Publication of the American Chemical Society*, 32: 2070–2077.
- [40] Thenuwara, A. C., Shetty, P. P., Kondekar, N., Sandoval, S. E., Cavallaro, K., May, R., Yang, C. T., Marbella, L. E., Qi, Y., McDowell, M. T. (2020). Efficient low-temperature cycling of lithium metal anodes by tailoring the solid-electrolyte interphase. *ACS Energy Letters*, 5: 2411–2420.
- [41] Thenuwara, A. C., Shetty, P. P., McDowell, M. T. (2019). Distinct nanoscale interphases and morphology of lithium metal electrodes operating at low temperatures. *Nano Letters*, 19: 8664–8672.
- [42] Li, B. Q., Kong, L., Zhao, C. X., Jin, Q., Chen, X., Peng, H. J., Qin, J. L., Chen, J. X., Yuan, H., Zhang, Q., et al. (2019). Expediting redox kinetics of sulfur species by atomic-scale electrocatalysts in lithium-sulfur batteries. *InfoMat*, 1: 533–541.
- [43] Zhao, C. X., Chen, W. J., Zhao, M., Song, Y. W., Liu, J. N., Li, B. Q., Yuan, T. Q., Chen, C. M., Zhang, Q., Huang, J. Q. (2021). Redox mediator assists electron transfer in lithium-sulfur batteries with sulfurized polyacrylonitrile cathodes. *EcoMat*, 3: e12066.
- [44] Pathak, R., Chen, K., Gurung, A., Reza, K. M., Bahrami, B., Pokharel, J., Baniya, A., He, W., Wu, F., Zhou, Y., et al. (2020). Fluorinated hybrid solid-electrolyte-interphase for dendrite-free lithium deposition. *Nature Communications*, 11: 93.
- [45] Chen, J., Fan, X., Li, Q., Yang, H., Khoshi, M. R., Xu, Y., Hwang, S., Chen, L., Ji, X., Yang, C., et al. (2020). Electrolyte design for LiF-rich solid-electrolyte interfaces to enable high-performance micro-sized alloy anodes for batteries. *Nature Energy*, 5: 386–397.
- [46] Zhao, C. Z., Duan, H., Huang, J. Q., Zhang, J., Zhang, Q., Guo, Y. G., Wan, L. J. (2019). Designing solid-state interfaces on lithium-metal anodes: A review. *Science China Chemistry*, 62: 1286–1299.
- [47] Yan, C., Yuan, H., Park, H. S., Huang, J. Q. (2020). Perspective on the critical role of interface for advanced batteries. *Journal of Energy Chemistry*, 47: 217–220.
- [48] Yang, Q. F., Li, C. L. (2018). Li metal batteries and solid state batteries benefiting from halogen-based strategies. *Energy Storage Materials*, 14: 100–117.
- [49] Yan, K., Wang, J. Y., Zhao, S. Q., Zhou, D., Sun, B., Cui, Y., Wang, G. X. (2019). Temperature-dependent nucleation and growth of dendrite-free lithium metal anodes. *Angewandte Chemie International Edition*, 58: 11364–11368.
- [50] Wang, J. Y., Huang, W., Pei, A., Li, Y. Z., Shi, F. F., Yu, X. Y., Cui, Y. (2019). Improving cyclability of Li metal batteries at elevated temperatures and its origin revealed by cryo-electron microscopy. *Nature Energy*, 4: 664–670.
- [51] Ishikawa, M., Tasaka, Y., Yoshimoto, N., Morita, M. (2001). Optimization of physicochemical characteristics of a lithium anode interface for high-efficiency cycling: An effect of electrolyte temperature. *Journal of Power Sources*, 97–98: 262–264.
- [52] Xu, K., von Cresce, A., Lee, U. (2010). Differentiating contributions to “ion transfer” barrier from interphasial resistance and Li⁺ desolvation at electrolyte/graphite interface. *Langmuir: the ACS Journal of Surfaces and Colloids*, 26: 11538–11543.
- [53] Yan, C., Yao, Y. X., Cai, W. L., Xu, L., Kaskel, S., Park, H. S., Huang, J. Q. (2020). The influence of formation temperature on the solid electrolyte interphase of graphite in lithium ion batteries. *Journal of Energy Chemistry*, 49: 335–338.
- [54] Akolkar, R. (2014). Modeling dendrite growth during lithium electrodeposition at sub-ambient temperature. *Journal of Power Sources*, 246: 84–89.
- [55] Lushta, V., Dietzel, D., Roling, B., Schirmeisen, A. (2019). Nanoscale characterization of ion mobility by temperature-controlled Li-nanoparticle growth. *ACS Applied Materials & Interfaces*, 11: 5476–5483.
- [56] Zhai, P. B., Liu, L. X., Gu, X. K., Wang, T. S., Gong, Y. J. (2020). Interface engineering for lithium metal anodes in liquid electrolyte. *Advanced Energy Materials*, 10: 2001257.
- [57] Jow, T. R., Delp, S. A., Allen, J. L., Jones, J. P., Smart, M. C. (2018). Factors limiting Li⁺ charge transfer kinetics in Li-ion batteries. *Journal of the Electrochemical Society*, 165: A361–A367.
- [58] Liu, T., Lin, L., Bi, X., Tian, L., Yang, K., Liu, J., Li, M., Chen, Z., Lu, J., Amine, K., et al. (2019). In situ quantification of interphasial chemistry in Li-ion battery. *Nature Nanotechnology*, 14: 50–56.
- [59] Mei, W. X., Jiang, L. H., Liang, C., Sun, J. H., Wang, Q. S. (2021). Understanding of Li-plating on graphite electrode: Detection, quantification and mechanism revelation. *Energy Storage Materials*, 41: 209–221.
- [60] Cai, W. L., Yao, Y. X., Zhu, G. L., Yan, C., Jiang, L. L., He, C. X., Huang, J. Q., Zhang, Q. (2020). A review on energy chemistry of fast-charging anodes. *Chemical Society Reviews*, 49: 3806–3833.
- [61] Wang, W., Liao, C., Liew, K. M., Chen, Z. H., Song, L., Kan, Y. C., Hu, Y. (2019). A 3D flexible and robust HAPs/PVA separator prepared by a freezing-drying method for safe lithium metal batteries. *Journal of Materials Chemistry A*, 7: 6859–6868.
- [62] Huo, H. Y., Chen, Y., Li, R. Y., Zhao, N., Luo, J., Pereira da Silva, J. G., Mücke, R., Kaghazchi, P., Guo, X. X., Sun, X. L. (2020). Design of a mixed conductive garnet/Li interface for dendrite-free solid lithium metal batteries. *Energy & Environmental Science*, 13: 127–134.
- [63] Cheng, X. B., Zhao, C. Z., Yao, Y. X., Liu, H., Zhang, Q. (2019). Recent advances in energy chemistry between solid-state electrolyte and safe lithium-metal anodes. *Chem*, 5: 74–96.
- [64] Shen, X., Zhang, R., Chen, X., Cheng, X. B., Li, X. Y., Zhang, Q. (2020). The failure of solid electrolyte interphase on Li metal anode: Structural uniformity or mechanical strength. *Advanced Energy Materials*, 10: 1903645.
- [65] Piao, N., Ji, X., Xu, H., Fan, X. L., Chen, L., Liu, S. F., Garaga, M. N., Greenbaum, S. G., Wang, L., Wang, C. S., et al. (2020). Countersolvent electrolytes for lithium-metal batteries. *Advanced Energy Materials*, 10: 1903568.
- [66] Motoyama, M., Ejiri, M., Iriyama, Y. (2015). Modeling the nucleation and growth of Li at metal current collector/LiPON interfaces. *Journal of the Electrochemical Society*, 162: A7067–A7071.
- [67] Xu, C., Ahmad, Z., Aryanfar, A., Viswanathan, V., Greer, J. R. (2017). Enhanced strength and temperature dependence of mechanical properties of Li at small scales and its implications for Li metal anodes. *Proceedings of the National Academy of Sciences of the United States of America*, 114: 57–61.
- [68] Cai, G. R., Holoubek, J., Xia, D. W., Li, M. Q., Yin, Y. J., Xing, X., Liu, P., Chen, Z. (2020). An ester electrolyte for lithium-sulfur batteries capable of ultra-low temperature cycling. *Chemical Communications (Cambridge, England)*, 56: 9114–9117.
- [69] Holoubek, J., Liu, H., Wu, Z., Yin, Y., Xing, X., Cai, G., Yu, S., Zhou, H., Pascal, T. A., Chen, Z., et al. (2021). Tailoring electrolyte solvation for Li metal batteries cycled at ultra-low temperature. *Nature Energy*, 6: 303–313.
- [70] Plichta, E. J., Behl, W. K. (2000). A low-temperature electrolyte for lithium and lithium-ion batteries. *Journal of Power Sources*, 88: 192–196.
- [71] Li, Q. Y., Jiao, S. H., Luo, L. L., Ding, M. S., Zheng, J. M., Cartmell, S. S., Wang, C. M., Xu, K., Zhang, J. G., Xu, W. (2017). Wide-temperature electrolytes for lithium-ion batteries. *ACS Applied Materials & Interfaces*, 9: 18826–18835.
- [72] Shanguan, X. H., Xu, G. J., Cui, Z. L., Wang, Q. L., Du, X. F., Chen, K., Huang, S. Q., Jia, G. F., Li, F. Q., Wang, X., et al. (2019). Additive-assisted novel dual-salt electrolyte addresses wide temperature operation of lithium-metal batteries. *Small*, 15: 1900269.
- [73] Dong, X. L., Lin, Y. X., Li, P. L., Ma, Y. Y., Huang, J. H., Bin, D., Wang, Y. G., Qi, Y., Xia, Y. Y. (2019). High-energy rechargeable metallic lithium battery at -70°C enabled by a cosolvent electrolyte. *Angewandte Chemie International Edition*, 58: 5623–5627.
- [74] Fan, X., Ji, X., Chen, L., Chen, J., Deng, T., Han, F., Yue, J., Piao, N., Wang, R., Zhou, X., et al. (2019). All-temperature batteries enabled by fluorinated electrolytes with non-polar solvents. *Nature Energy*, 4: 882–890.
- [75] Ren, X. D., Chen, S. R., Lee, H., Mei, D. H., Engelhard, M. H., Burton, S. D., Zhao, W. G., Zheng, J. M., Li, Q. Y., Ding, M. S., et al. (2018). Localized high-concentration sulfone electrolytes for

- high-efficiency lithium-metal batteries. *Chem*, 4: 1877–1892.
- [76] Rustomji, C. S., Yang, Y., Kim, T. K., Mac, J., Kim, Y. J., Caldwell, E., Chung, H., Meng, Y. S. (2017). Liquefied gas electrolytes for electrochemical energy storage devices. *Science*, 356: eaal4263.
- [77] Yang, Y., Yin, Y. J., Davies, D. M., Zhang, M. H., Mayer, M., Zhang, Y. H., Sablina, E. S., Wang, S., Lee, J. Z., Borodin, O., et al. (2020). Liquefied gas electrolytes for wide-temperature lithium metal batteries. *Energy & Environmental Science*, 13: 2209–2219.
- [78] Yao, Y. X., Chen, X., Yan, C., Zhang, X. Q., Cai, W. L., Huang, J. Q., Zhang, Q. (2021). Regulating interfacial chemistry in lithium-ion batteries by a weakly solvating electrolyte. *Angewandte Chemie International Edition*, 60: 4090–4097.
- [79] Hu, D. Z., Chen, G., Tian, J., Li, N., Chen, L., Su, Y. F., Song, T. L., Lu, Y., Cao, D. Y., Chen, S., et al. (2021). Unrevealing the effects of low temperature on cycling life of 21700-type cylindrical Li-ion batteries. *Journal of Energy Chemistry*, 60: 104–110.
- [80] Li, S., Li, Z. D., Huai, L. Y., Ma, M. M., Luo, K. L., Chen, J. H., Wang, D. Y., Peng, Z. (2021). A strongly interactive adatom/substrate interface for dendrite-free and high-rate Li metal anodes. *Journal of Energy Chemistry*, 62: 179–190.
- [81] Jiang, L. L., Yan, C., Yao, Y. X., Cai, W. L., Huang, J. Q., Zhang, Q. (2021). Inhibiting solvent co-intercalation in a graphite anode by a localized high-concentration electrolyte in fast-charging batteries. *Angewandte Chemie International Edition*, 60: 3402–3406.
- [82] Meng, J. W., Lei, M., Lai, C. Z., Wu, Q. P., Liu, Y. Y., Li, C. L. (2021). Lithium ion repulsion-enrichment synergism induced by core-shell ionic complexes to enable high-loading lithium metal batteries. *Angewandte Chemie International Edition*, 60: 23256–23266.
- [83] Jiang, G. X., Li, F., Wang, H. P., Wu, M. G., Qi, S. H., Liu, X. H., Yang, S. C., Ma, J. M. (2021). Perspective on high-concentration electrolytes for lithium metal batteries. *Small Structures*, 2: 2000122.
- [84] Liu, Y., Zhai, Y. P., Xia, Y. Y., Li, W., Zhao, D. Y. (2021). Recent progress of porous materials in lithium-metal batteries. *Small Structures*, 2: 2000118.
- [85] Gao, Y., Rojas, T., Wang, K., Liu, S., Wang, D. W., Chen, T. H., Wang, H. Y., Ngo, A. T., Wang, D. H. (2020). Low-temperature and high-rate-charging lithium metal batteries enabled by an electrochemically active monolayer-regulated interface. *Nature Energy*, 5: 534–542.
- [86] Adair, K. R., Banis, M. N., Zhao, Y., Bond, T., Li, R. Y., Sun, X. L. (2020). Temperature-dependent chemical and physical microstructure of Li metal anodes revealed through synchrotron-based imaging techniques. *Advanced Materials*, 32: 2002550.
- [87] Maraschky, A., Akolkar, R. (2020). Temperature dependence of dendritic lithium electrodeposition: A mechanistic study of the role of transport limitations within the SEI. *Journal of the Electrochemical Society*, 167: 062503.
- [88] Xiao, P. T., Luo, R. P., Piao, Z. H., Li, C., Wang, J. X., Yu, K., Zhou, G. M., Cheng, H. M. (2021). High-performance lithium metal batteries with a wide operating temperature range in carbonate electrolyte by manipulating interfacial chemistry. *ACS Energy Letters*, 6: 3170–3179.
- [89] Holoubek, J., Yu, M. Y., Yu, S. C., Li, M. Q., Wu, Z. H., Xia, D. W., Bhaladhare, P., Gonzalez, M. S., Pascal, T. A., Liu, P., et al. (2020). An all-fluorinated ester electrolyte for stable high-voltage Li metal batteries capable of ultra-low-temperature operation. *ACS Energy Letters*, 5: 1438–1447.
- [90] Gao, Y., Wang, D. W., Shin, Y. K., Yan, Z. F., Han, Z., Wang, K., Hossain, M. J., Shen, S. L., AlZahrani, A., van Duin, A. C. T., et al. (2020). Stable metal anodes enabled by a labile organic molecule bonded to a reduced graphene oxide aerogel. *Proceedings of the National Academy of Sciences of the United States of America*, 117: 30135–30141.
- [91] Yan, C., Jiang, L. L., Yao, Y. X., Lu, Y., Huang, J. Q., Zhang, Q. (2021). Nucleation and growth mechanism of anion-derived solid electrolyte interphase in rechargeable batteries. *Angewandte Chemie International Edition*, 60: 8521–8525.
- [92] Cai, W. L., Yan, C., Yao, Y. X., Xu, L., Chen, X. R., Huang, J. Q., Zhang, Q. (2021). The boundary of lithium plating in graphite electrode for safe lithium-ion batteries. *Angewandte Chemie International Edition*, 60: 13007–13012.
- [93] Shen, X., Cheng, X. B., Shi, P., Huang, J. Q., Zhang, X. Q., Yan, C., Li, T., Zhang, Q. (2019). Lithium-matrix composite anode protected by a solid electrolyte layer for stable lithium metal batteries. *Journal of Energy Chemistry*, 37: 29–34.
- [94] Ding, J. F., Xu, R., Yan, C., Li, B. Q., Yuan, H., Huang, J. Q. (2021). A review on the failure and regulation of solid electrolyte interphase in lithium batteries. *Journal of Energy Chemistry*, 59: 306–319.
- [95] Yao, Y. X., Zhang, X. Q., Li, B. Q., Yan, C., Chen, P. Y., Huang, J. Q., Zhang, Q. (2020). A compact inorganic layer for robust anode protection in lithium-sulfur batteries. *InfoMat*, 2: 379–388.
- [96] Li, T., Zhang, X. Q., Yao, N., Yao, Y. X., Hou, L. P., Chen, X., Zhou, M. Y., Huang, J. Q., Zhang, Q. (2021). Stable anion-derived solid electrolyte interphase in lithium metal batteries. *Angewandte Chemie International Edition*, 60: 22683–22687.
- [97] Shen, X., Zhang, R., Wang, S. H., Chen, X., Zhao, C., Kuzmina, E., Karaseva, E., Kolosnitsyn, V., Zhang, Q. (2021). The dynamic evolution of aggregated lithium dendrites in lithium metal batteries. *Chinese Journal of Chemical Engineering*, 37: 137–143.
- [98] Zhang, Q. K., Liu, S., Lu, Y. T., Xing, L. D., Li, W. S. (2021). Artificial interphases enable dendrite-free Li-metal anodes. *Journal of Energy Chemistry*, 58: 198–206.
- [99] Xu, R., Cheng, X. B., Yan, C., Zhang, X. Q., Xiao, Y., Zhao, C. Z., Huang, J. Q., Zhang, Q. (2019). Artificial interphases for highly stable lithium metal anode. *Matter*, 1: 317–344.
- [100] Chen, X. R., Yan, C., Ding, J. F., Peng, H. J., Zhang, Q. (2021). New insights into “dead lithium” during stripping in lithium metal batteries. *Journal of Energy Chemistry*, 62: 289–294.
- [101] Wei, C. L., Tan, L. W., Tao, Y., An, Y. L., Tian, Y., Jiang, H. Y., Feng, J. K., Qian, Y. T. (2021). Interfacial passivation by room-temperature liquid metal enabling stable 5 V-class lithium-metal batteries in commercial carbonate-based electrolyte. *Energy Storage Materials*, 34: 12–21.
- [102] Zeng, J. K., Liu, Q. T., Jia, D. Y., Liu, R. L., Liu, S. H., Zheng, B. N., Zhu, Y. L., Fu, R. W., Wu, D. C. (2021). A polymer brush-based robust and flexible single-ion conducting artificial SEI film for fast charging lithium metal batteries. *Energy Storage Materials*, 41: 697–702.
- [103] Shen, X., Zhang, R., Shi, P., Chen, X., Zhang, Q. (2021). How does external pressure shape Li dendrites in Li metal batteries? *Advanced Energy Materials*, 11: 2003416.
- [104] Wang, J., Yang, M., Zou, G., Liu, D., Peng, Q. (2021). Lithiation MXene derivative skeletons for wide-temperature lithium metal anodes. *Advanced Functional Materials*, 31: 2101180.
- [105] Rashad, M., Asif, M. (2021). Understanding the low temperature electrochemistry of magnesium-lithium hybrid ion battery in all-phenyl-complex solutions. *Journal of Energy Chemistry*, 56: 383–390.
- [106] Krauskopf, T., Mogwitz, B., Rosenbach, C., Zeier, W. G., Janek, J. (2019). Diffusion limitation of lithium metal and Li-Mg alloy anodes on LLZO type solid electrolytes as a function of temperature and pressure. *Advanced Energy Materials*, 9: 1902568.
- [107] Lu, Y., Zhao, C. Z., Zhang, R., Yuan, H., Hou, L. P., Fu, Z. H., Chen, X., Huang, J. Q., Zhang, Q. (2021). The carrier transition from Li atoms to Li vacancies in solid-state lithium alloy anodes. *Science Advances*, 7: eabi5520.
- [108] García, G., Dieckhöfer, S., Schuhmann, W., Ventosa, E. (2018). Exceeding 6500 cycles for LiFePO₄/Li metal batteries through understanding pulsed charging protocols. *Journal of Materials Chemistry A*, 6: 4746–4751.
- [109] Li, Q., Tan, S., Li, L., Lu, Y., He, Y. (2017). Understanding the molecular mechanism of pulse current charging for stable lithium-metal batteries. *Science Advances*, 3: e1701246.
- [110] Hope, M. A., Rinkel, B. L. D., Gunnarsdóttir, A. B., Märker, K., Menkin, S., Paul, S., Sergeyev, I. V., Grey, C. P. (2020). Selective NMR observation of the SEI–metal interface by dynamic nuclear polarisation from lithium metal. *Nature Communications*, 11: 2224.