

Advancements in Low-Temperature Lithium Metal Batteries: A Comprehensive Review

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Abstract. Lithium metal batteries (LMB) represent a major advance in energy storage technology, offering a huge high energy density, and have the potential to be used in important fields such as electric vehicles and aerospace. However, their practical application at low temperatures still faces major challenges. This paper reviews recent advances in overcoming these obstacles, including the development of ether-based and fluorated electrolytes to reduce dendrite formation, improve SEI stability, and the use of 3D collectors and protective coatings to create more stable interfaces. By combining these methods, we conclude from a large number of studies that the problem of LMB at low temperatures is not the result of a single aspect, but the result of multiple factors. SEI instability leads to uneven lithium deposition and electrolyte decomposition in LMB. At the same time, the ionic conductivity of the electrolyte decreases at low temperature, slowing down the transmission rate of lithium ions, resulting in an increase in overpotential and promoting the uneven deposition of lithium. Therefore, this paper proposed a feasible path for the future development of LMB, that is, strengthening the three-dimensional lipophilic skeleton while improving the electrolyte solution, and constructing the three-dimensional lipophilic skeleton of SEI to solve the problems of lithium dendrite growth of LMB at low temperature and SEI instability.

Keywords: Lithium dendrite growth, Electrode design, Electrolyte formulation, Low temperature.

1. Introduction

From the moment lithium metal batteries (LMB) appeared, LMB began to meet people's needs for high energy density batteries that can operate at low temperatures. In particular, it provides a viable alternative for multiple uses of batteries in extreme environments, including aerospace technology and new energy vehicles. But there are still several major hurdles to overcome before LMB can be put to practical use. Therefore, this study focuses on three major problems of LMB - solid electrolyte interface (SEI) stability, lithium dendrite growth, and overall low temperature performance, and this paper discusses the latest progress to date in addressing these difficulties. In general, due to the advantages of low electrochemical potential and high theoretical energy density of lithium metal batteries themselves, they are considered to be the new direction of the next generation of energy storage technology. Xu et al. pointed out that unlike other traditional lithium-ion batteries (LiBs) that use graphite anodes, LMB batteries use lithium metal as the anode, and this change in electrode structure significantly increases the energy density of LMB batteries [1]. This makes them suitable for applications that require long-life and lightweight power supplies, such as electric vehicles and aerospace systems.

However, in practice LMB is hampered by several key issues. One of the main challenges is the growth of lithium dendrites, especially during the electrical cycle. The research of Sun et al and Zou et al showed that these dendrite structures could penetrate the membrane and cause short circuit of the battery, resulting in catastrophic failure and safety hazards [2-3]. One point of concern is that the problem of dendrite growth will be exacerbated at low temperatures, when the ionic conductivity will be reduced, resulting in more uneven lithium plating [4].

At the same time, another challenge is the stability of the solid electrolyte interface (SEI). First of all, by understanding the formation and production of SEI, it can be known that SEI is an inactive protective layer formed on the surface of the lithium anode during the process of battery discharge

and charging, which plays a crucial role in the performance and life of the battery. This is because a stable SEI prevents the electrolyte in the LMB from continuously breaking down and at the same time ensures efficient lithium-ion transport. However, Xu et al and Sun et al discussed that SEI is prone to become unstable at low temperature, so the result of SEI instability is increased resistance and shortened battery life [1-2]. So, in the future, the research focus can be placed on the dynamic characteristics of SEI, especially the dynamic characteristics under low temperature and repeated circulation pressure [4].

Considering that the negative effects of lithium dendrite growth and solid electrolyte interface (SEI) stability include reduced ionic conductivity, increased polarization, and slowed lithium-ion transport, these negative effects further hinder the overall performance of LMB at low temperatures. At the same time, Wang et al and Zhang et al mentioned that the consequences brought by these problems together lead to the low efficiency of LMB batteries and the attenuation of battery capacity at low temperatures [5-6]. Therefore, in the current study, the direction of research is to solve the lithium dendrite growth and SEI stability in LMB batteries through an integrated approach, the main solutions include optimization of electrolyte formulation, improvement of SEI stability and innovative electrode design (show in Figure 1).

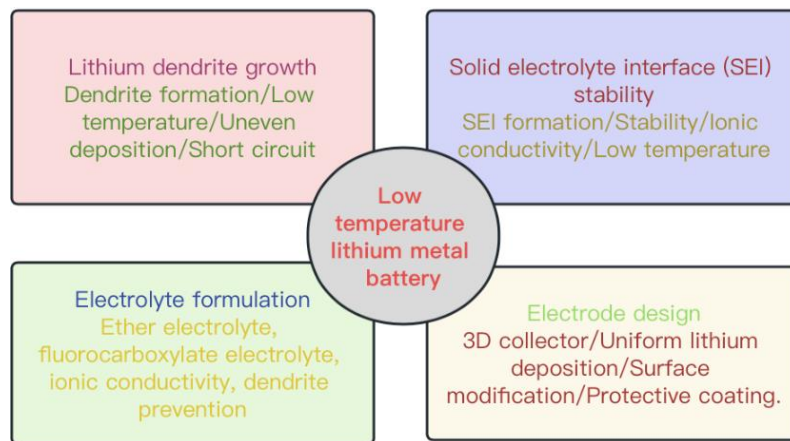


Figure 1. The problems and theme of lithium battery at low temperature.

2. Lithium dendrite growth

2.1. Explain the fundamental problem of lithium dendrite growth in LMB

Lithium metal batteries (LMB) have been widely recognized in recent years for their high energy density and great potential in transforming energy storage systems. However, the growth of lithium dendrites has become the biggest challenge hindering its widespread market availability. Thenuwara et al and Zou et al have shown that during the electrical cycle of lithium anode, needle-like structures will be formed on its surface, which are called dendrites, which can penetrate the diaphragm and cause short circuit. Therefore, the existence of dendrites will cause serious safety risks for LMB batteries [3,7].

During the charging process, the uneven deposition of lithium ions often leads to the accelerated growth of lithium dendrites. Reviewing the discussion on lithium-ion dendrites by Thenuwara et al and Zou et al, it can be concluded that current density, electrolyte composition, anode surface characteristics and other factors are the main causes of uneven lithium deposition, and once uneven lithium deposition occurs, dendrite structure will be exacerbated on the surface of lithium anode [3,7]. At the same time, the formation of these dendrites will not only reduce the capacity and efficiency of the battery, but also increase the possibility of short circuits inside the LMB battery, leading to thermal runaway and fire.

2.2. How to accelerate dendrite formation at low temperature

It is noteworthy that the problem of lithium dendrite growth is significantly aggravated at low temperature. Gao et al described that with the decrease of temperature, the ionic conductivity of electrolytes in LMB will decrease, resulting in a slower transport rate of lithium ions ^[4]. At the same time, this slow internal motion leads to higher overpotential in the LMB, which tends to accelerate the uneven deposition of lithium, thus promoting the formation of dendrites. In addition, at low temperatures, the viscosity of the electrolyte increases, which further hinders the transport of lithium ions and leads to the formation of dendritic structures ^[3].

At low temperatures, the solid electrolyte interface (SEI) on the lithium anode in the LMB becomes unstable, and the effect is that the SEI becomes more prone to cracking. In addition, the continuous electrolyte decomposition caused by this instability in the SEI layer will lead to uneven lithium deposition, which creates favorable conditions for dendrite growth, resulting in accelerated growth of lithium dendrite and destruction of the internal structure of LMB ^[4]. In general, the instability of SEI at low temperatures is the main reason that causes it to become vulnerable at low temperatures. Once SEI becomes vulnerable, it means that it cannot effectively prevent dendrite penetration, and the result will increase the safety of LMB in cold environments.

According to recent studies, the use of 3D Li-philic frameworks, such as Ni-NiO, in LMB's lithium anodes helps regulate lithium deposition in low temperature environments and effectively slow dendrite growth ^[8]. The principle behind these structures is to provide a more uniform and stable surface for the lithium anode, which has the benefit of contributing to the uniform distribution of lithium ions, thereby preventing the formation of dendrites. Wang et al discussed that the abundant grain boundaries on the surface of 3D Ni-NiO structure can allow adhesion and formation of SEI layer, while maintaining or enhancing ionic conductivity at low temperature ^[8]. They also reported that the abundant grain boundaries of the SEI layer under this structure would show a lower Li⁺ transport barrier, which is more conducive to uniform Li deposition. Therefore, it can be found that the 3D Ni-NiO structure plays a crucial role in maintaining the stability of the SEI, and it can also be considered that it reduces the tendency of dendrite formation ^[8].

The growth of lithium dendrites in LMB is a fundamental problem that is difficult to solve, because the decrease of ionic conductivity, the increase of electrolyte viscosity and the instability of SEI formation make LMB unable to maintain the original normal working efficiency at low temperatures. A multifaceted approach can be taken to address these challenges, including designing materials and adjusting electrolyte formulations by promoting uniform deposition of lithium and improving the stability of the SEI layer.

2.3. Electrolyte formulation

One of the most effective strategies to mitigate dendrite growth in lithium metal batteries (LMB) is to improve and formulate advanced electrolytes. Thenuwara et al. studied ether-based electrolytes composed of 1, 3-dioxane (DOL) and 1, 2-dimethoxy-ethane (DME), which showed great potential in reducing dendrite formation ^[7]. According to his research, after using DOL/DME electrolyte combined with LiTFSI, ionic conductivity at -80°C can be as high as ~0.4 mS cm⁻¹ ^[7]. Therefore, it can be hypothesized that lithium deposition in LMB can be smoother and more uniform with the use of DOL/DME electrolyte, thus minimizing dendrite penetration. In summary, DOL/DME, an ether-based electrolyte, can promote more uniform lithium deposition in LMB by enhancing ionic conductivity and reducing electrolyte viscosity at low temperatures.

In addition to ether-based electrolytes, fluorocarboxylate electrolytes (FCE) can also be used as another effective solution to slow dendrite growth. The adopted electrolytes of diethyl fluoropropionate (DEFM) and vinyl fluorocarbonate (FEC) can form a stable solid electrolyte interface (SEI) rich in inorganic components such as LiF by promoting the solvation structure dominated by Li anion ^[3]. Zou et al showed that this SEI provides better passivation and stability, so

that during the cycle, the FCE electrolyte exhibits high ionic conductivity and stable cycling properties at low temperatures [3].

In general, the adjustment and configuration of novel electrolyte formulations, such as ether-based and fluorocarboxylate electrolytes, can significantly improve lithium deposition and reduce dendrite formation. At the same time, it can be found in continuous attempts and research that protective coatings can be used directly on lithium metal anodes to prevent the growth of dendrites.

2.4. Surface modification

Surface modification of lithium metal anode can be used as an effective strategy to prevent dendrite growth and improve battery performance. One of the limited methods is to use a protective coating, such as polydopamine coated $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.2}\text{O}_{12}$ (PDA@LLZTO). Wang et al claimed that the coating forms a stable and uniform layer on the surface of the lithium anode, which plays a crucial role in regulating the deposition of lithium ions and preventing dendrite formation [5]. The principle of action of the coating can be described as a polydopamine (PDA) layer acting as a bonding interface that binds the lithium metal to LLZTO's ceramic particles, resulting in a composite structure that is both mechanically robust and chemically stable [5].

PDA@LLZTO coatings significantly improve the stability of the solid electrolyte interface (SEI) by providing a special protective barrier against electrolyte decomposition, while at the same time, the barrier reduces the reactivity of the lithium surface, thereby minimizing the formation of lithium dendrites [5]. In addition, the Lipophilic properties of PDA and the high ionic conductivity of LLZTO particles promote uniform flow transport of lithium ions during the cycle, which contributes to smooth, uniform lithium deposition [5]. By preventing the locally high current density that leads to dendrite growth, these coatings ensure that lithium metal batteries operate more safely and efficiently, especially at low temperatures where dendrite formation is more common.

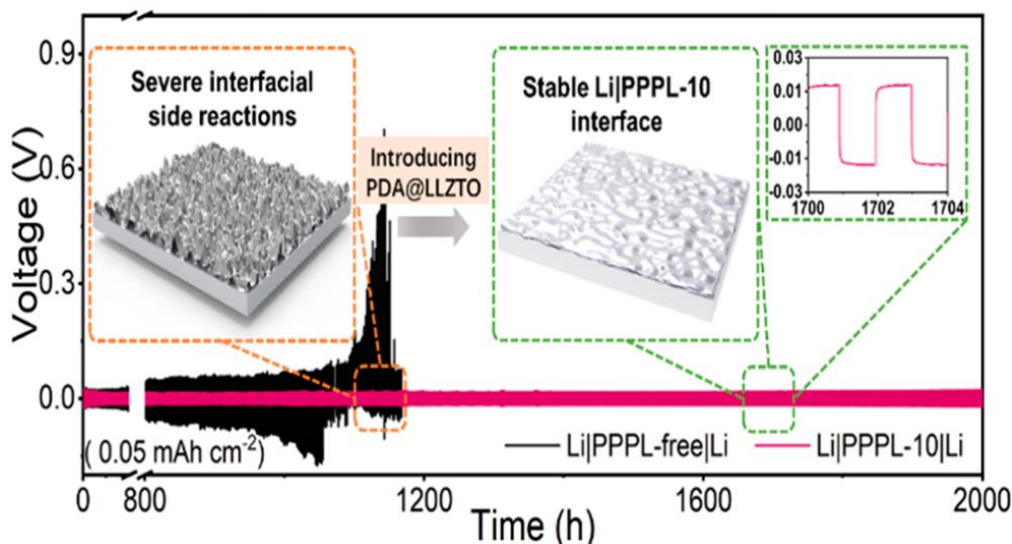


Figure 2. The figure shows the voltage change over time for two different configurations of lithium metal batteries (LMB). It compared the performance of the Li|PPPL-free|Li battery with that of the Li|PPPL-10|Li battery with a polydopamine coating $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.2}\text{O}_{12}$ (PDA@LLZTO) [5].

The severe interface side reactions can be seen in Figure 2 by comparing the two different LMB. Li|PPPL-free| the Li battery (black line) exhibits severe interface side reactions, with significant voltage fluctuations and instability after about 800 hours of operation. In comparison, the Li|PPPL-10 interface is relatively stable, because its Li|PPPL-10|Li battery (pink wire) with PDA@LLZTO coating shows stable voltage for a longer time (up to 2000 hours), indicating increased stability and reduced side reactions. In addition, compared with the voltage stability, the voltage of the Li|PPPL-10|Li battery remains close to 0 V, which indicates that the introduction of PDA@LLZTO coating

significantly improves the interface stability and prevents large voltage spikes in the Li|PPPL-free|Li battery ^[5].

In summary, the use of the polydopamine coating $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.2}\text{O}_{12}$ as a protective layer for lithium metal anodes results in a stable interface, which is essential for alleviating dendrite growth. These coatings enhance the mechanical and chemical stability of the SEI, promote uniform deposition of lithium, and significantly improve the overall performance and safety of lithium metal batteries.

It is worth noting that an innovative strategy to slow the growth of lithium dendrites has recently emerged, which is to expose lithium metal to air for a short period of time to form a controlled oxidation protective layer on the surface of lithium metal. This method contrasts with the traditional method of separating lithium metal from oxygen-containing substances. By allowing lithium metal to react with air, a dense uniform protective layer composed of Li_3N , Li_2O , LiOH and Li_2CO_3 can be formed on its surface ^[9]. This layer can be used as a passivation film, and the film is very hard, which is conducive to enhancing the stability and performance of lithium metal anodes, especially at low temperatures. Zheng et al. 's research shows that air-treated lithium metal has excellent dendrite inhibition performance ^[9]. After air pretreatment, the lithium metal battery can still maintain a high life of 4500 hours at -30°C . Meanwhile, studies have shown that the voltage polarization is significantly reduced at -20°C , which indicates that the dendrite growth problem has been effectively alleviated ^[9]. In addition, Zheng et al also mentioned that the full battery using lithium metal after air pretreatment as the anode and NCM811 as the cathode can still maintain high efficiency at -20°C and -40°C ^[9]. This simple, low-cost approach offers a promising solution for the development of high-performance lithium metal batteries suitable for a wide temperature range, while also addressing the key problem of dendrite growth in LMB.

3. Solid electrolyte interface (SEI) stability

3.1. Importance of Solid electrolyte interface (SEI)

Solid electrolyte interface (SEI) is one of the important factors affecting the performance and life of lithium metal battery (LMB). During the initial electrical cycle of the LMB battery, SEI will form on the surface of the lithium anode as a protective layer, and at the same time, it will act as a protective barrier between the electrolyte and the lithium metal to effectively prevent the electrolyte from continuing to decompose and ensure the efficient transmission of lithium ions ^[1]. A stable SEI is essential for uniform lithium deposition, as a stable SEI minimizes dendrite formation to prevent short circuits and failures of the battery. However, it is worth noting that at low temperatures, the SEI layer becomes particularly unstable, which leads to an increase in resistance and a decrease in battery life. To analyze the reasons why SEI becomes unstable, it can be found that this instability is caused by the decrease of ionic conductivity and the increase of brittleness of SEI at lower temperatures, which leads to the rupture and degradation of SEI during the electrical cycle. The unstable SEI layer will accelerate the growth of lithium dendrites, which further compromises the safety and efficiency of LMB ^[1]. Zou et al tried to add fluorine compounds, such as diethyl fluoropropionate (DEFM) and vinyl fluorocarbonate (FEC), to the electrolyte to enhance SEI stability and ionic conductivity, thereby improving the low-temperature performance of the battery ^[3]. In addition, Zheng et al 's research shows that SEI formed by moderate exposure of lithium metal to air is rich in Li_3N and Li_2CO_3 lithium-based compounds, which have a strong protective effect at sub-zero temperatures and can improve electrochemical performance ^[6]. Therefore, maintaining a stable SEI is critical to developing a high-performance LMB that can operate efficiently under extreme conditions.

3.2. Progress in SEI stability - SEI Composition

Recent studies have made significant progress in forming stable solid electrolyte interfaces (SEI) for lithium metal batteries (LMB) and enhancing SEI stability by synthesizing inorganic components rich in lithium fluoride (LiF). LiF in SEI is critical because it provides high mechanical strength, excellent ionic conductivity, and chemical stability, all of which are necessary to maintain the long-term stable

performance of LMB^[5]. Fluorine-rich electrolytes play a crucial role in facilitating the formation of these sturdy SEI. Electrolytes containing fluorinated compounds, such as vinyl fluorocarbonate (FEC) and diethyl fluoropropionate (DEFM), break down to form SEI protective layers rich in LiF and other inorganic substances during the initiation of the electrical cycle^[3]. Because this fluorine-rich SEI layer can effectively passivate the lithium metal surface, it successfully prevents the continuous decomposition of the electrolyte and reduces the possibility of lithium dendrite formation. In addition, studies by Zou et al have shown that these fluorinated electrolytes enhance SEI stability and ionic conductivity and thus improve battery performance, especially at low temperatures^[3]. Using fluorine-rich electrolytes and adding inorganic components such as LiF ensures that the LMB forms a more uniform and stable SEI, which is essential for the LMB to be able to maintain efficient operation under a variety of environmental conditions. At the same time, the importance of electrolyte engineering in the development of the next generation energy storage system is emphasized once again.

3.3. Anion-derived SEI

The use of high concentration electrolytes (HCE) and local high concentration electrolytes (LHCE) has become an effective strategy for synthesizing robust and uniform solid electrolyte interfaces (SEI) in lithium metal batteries (LMB). Sun et al and Xu et al reported that HCE and LHCE promote the formation of SEI by increasing the concentration of lithium salts to promote anion derivation, and at the same time, these SEI are also rich in inorganic compounds such as lithium fluoride (LiF) and lithium nitrate (Li₃N)^[1-2]. According to the analysis, these anion-derived SEI have excellent mechanical strength, high ionic conductivity and chemical stability, which are critical for improving the performance and lifetime of LMB.

Xu et al. described that the uniform and stable coating provided by anion-derived SEI can effectively passivate the lithium metal surface and prevent the continuous decomposition of the electrolyte in LMB, while minimizing the formation of lithium dendrites^[1]. This is particularly important at low temperatures, where the stability of the SEI is challenged by reduced ionic conductivity and fragility, but the addition of anion-derived substances to the SEI using HCE and LHCE creates a more uniform protective layer on the surface of the lithium metal. This allows it to withstand the pressure of continuous electrical cycling and temperature changes^[1, 2]. After the successful synthesis of SEI using HCE and LHCE and using anion derivation, this SEI can be used to try to develop more reliable and efficient LMB.

3.4. Dynamic SEI formation

The dynamic characteristics of solid electrolyte interface (SEI) formation have a critical impact on the performance and life of lithium metal batteries (LMB). Because the SEI formation process is not static, it is constantly changing during the battery cycle, especially at low temperature pressure. This ongoing evolution directly affects the structural integrity of the SEI and its ability to effectively protect the lithium anode. At low temperatures, SEI easily becomes brittle and cracks, which leads to increased LMB resistance and shortened battery life. Therefore, understanding the dynamic behavior of the SEI is critical to developing long-term stable strategies.

Molecular dynamics simulations have become a powerful technique for studying SEI formation and behavior at the atomic level. These simulations provide insights into how different electrolyte compositions and environmental conditions affect SEI performance. For example, they can model the interaction between lithium ions, electrolyte molecules, and the anode surface, and thus reveal how temperature changes affect the stability of the SEI^[1]. Collectively, these simulations help identify the mechanisms behind SEI degradation and guide the development of more robust SEI layers.

Xu et al and Sun et al obtained SEI rich in inorganic compounds such as LiF and Li₃N by high concentration electrolyte (HCE) and local high concentration electrolyte (LHCE)^[1-2]. Experiments show that SEI can maintain its integrity well under dynamic cyclic conditions. At the same time, the

use of fluorine-rich electrolytes promotes the formation of these stable inorganic components, further improving the durability and ionic conductivity of SEI. The performance and reliability of LMB at low temperature can be improved by molecular dynamics simulation while understanding and optimizing SEI formation.

4. Low temperature performance

4.1. LMB challenges at low temperatures

The problems faced by lithium metal batteries (LMB) when working at low temperatures have seriously affected their performance and reliability. One of the main factors is the lower ionic conductivity of the electrolyte at low temperatures ^[4]. At the same time, with the decrease of temperature, the viscosity of electrolyte will increase, which will lead to the slow transport rate of lithium ions and the increase of internal resistance ^[10]. Therefore, after the reduction of ionic conductivity, the consequences include an increase in polarization (voltage difference), which greatly reduces the energy efficiency of the battery and also increases the formation of lithium dendrites.

In addition, the instability of the solid electrolyte interface (SEI) at low temperatures can lead to increased resistance and reduced battery capacity. Thenuwara et al showed that SEI was prone to brittle cracking under cold conditions, which would greatly reduce the capacity and life of the battery ^[7]. Therefore, the overall impact of solid electrolyte interface (SEI) instability on LMB performance includes low efficiency, fast capacity decay, and low stability, which makes maintaining reliable operation in cold environments challenging for future development of LMB.

Advanced electrolyte formulations and surface modifications can be used to alleviate these problems. For example, the use of fluorinated electrolytes and protective coatings on lithium anodes can enhance SEI stability and improve ionic conductivity at low temperatures. In addition, the addition of a high concentration electrolyte (HCE) and a locally high concentration electrolyte (LHCE) contributes to the formation of a strong anion-derived SEI that maintains the normal operation of the LMB even in cold conditions.

4.2. Electrode design

The future direction of lithium metal battery development can be placed on the development of advanced electrode designs, as they play a crucial role in improving the performance of lithium metal batteries (LMB), especially at low temperatures. In the study of Wang et al, the 3D collector they used is an effective method, and the collector made of Ni-NiO can provide a stable and uniform surface for lithium deposition ^[8]. These 3D lithiophile scaffolds help regulate the deposition and stripping of lithium in such a way that they reduce the possibility of dendrite formation by distributing lithium ions more evenly across the electrode surface. It can be analyzed from the results of Wang et al, that the increase of 3D collector surface area and structural stability improve the overall efficiency of lithium deposition, which can improve the performance of the battery and extend the cycle life even under low temperature environment ^[8].

In addition to this, another method that combines 3D collectors with an optimized electrolyte formulation can significantly improve LMB's low temperature performance. Guo et al 's research shows that at a low temperature of -30°C, 3D Ni-NiO foam collector combined with customized electrolytic liquid phase can effectively improve battery capacity and thus produce higher cycle performance ^[11]. In addition, existing studies have shown that the ester-based electrolyte can be extended to the working range of LMB at low temperatures, which will help to further improve the performance and stability of LMB ^[11]. Therefore, this design method can not only improve the efficiency of lithium plating and stripping, but also alleviate the resistance increase and capacity decay problems associated with cold environments. Overall, by providing a stable SEI interface and uniform lithium deposition, this advanced electrode design can effectively improve the overall life and reliability of the LMB, making it more suitable for applications in extreme conditions.

Overall, combining a 3D collector with an optimized electrolyte formulation proved effective in improving LMB's low temperature performance. Liu et al discussed that 3D collector provides a larger surface area and more uniform electric field distribution, effectively realizing uniform deposition of Li and preventing dendrite formation ^[12]. In addition, they are combined with electrolytes suitable for low temperature conditions (e.g., low temperature electrolyte: DOL/DME, which maintains a high ionic conductivity even at -80 ° C, with a value of about 0.4 mS/cm). Therefore, by mitigating the increased impedance and polarization effects at low temperatures, the overall performance can be further improved ^[12].

5. Conclusion and outlook

Whether lithium metal batteries (LMB) in low-temperature environments can ultimately achieve decisive breakthroughs and success depends on whether the challenges of lithium dendrite growth, SEI stability and overall low-temperature performance are solved. Due to the low ionic conductivity of LMB at low temperatures, the instability of the SEI layer, and the accelerated formation of dendrites and other basic problems, LMB can cause increased resistance and shortened battery life due to these problems. Current approaches that can effectively address these problems include electrolyte formulations that use ether-based solvents such as DOL/DME and fluorocarboxylate to reduce dendrite formation and improve SEI stability. Alternatively, surface modification methods, such as polydopamine coated with $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.2}\text{O}_{12}$ (PDA@LLZTO), can form a stable interface and prevent dendrite growth, thus significantly improving the low temperature performance of LMB. In addition, the use of 3D collector fluids, such as the Ni-NiO skeleton, can effectively regulate lithium deposition and reduce dendrite formation. As for high concentration electrolytes (HCE) and locally high concentration electrolytes (LHCE), they can further improve the stability of the SEI because the anion-derived SEI formed by these electrolytes are rich in inorganic compounds such as LiF and Li_3N . These SEI provide a uniform, stable layer that improves battery performance and life even at low temperatures. The combination of these advanced strategies and materials significantly improves the performance and stability of LMB at low temperatures. Continued research and innovation in electrolyte formulation, SEI stability, and electrode design are critical to developing reliable, high-performance LMB that can operate efficiently under extreme conditions. Future studies should aim to develop advanced characterization techniques to uncover interfacial processes, optimize materials and strategies, and attempt to verify the feasibility of constructing an SEI 3D oil-wet skeleton using a modified electrolyte solution in conjunction with a 3D oil-wet skeleton to address lithium dendrite growth and SEI instability at LMB low temperatures. It is expected that with continued innovation, LMB will meet the needs of a variety of applications ranging from electric vehicles to space exploration, where low temperature operation is critical.

References

- [1] Xu, R.; Zhang, S.; Shen, X.; Yao, N.; Ding, J.-F.; Xiao, Y.; Xu, L.; Yan, C.; Huang, J.-Q. Unlocking the Polarization and Reversibility Limitations for Stable Low-Temperature Lithium Metal Anodes[J]. *Small structures* 2023, 4 (7). <https://doi.org/10.1002/ssstr.202200400>.
- [2] Sun, N.; Li, R.; Zhao, Y.; Zhang, H.; Chen, J.; Xu, J.; Li, Z.; Fan, X.; Yao, X.; Peng, Z. Anionic Coordination Manipulation of Multilayer Solvation Structure Electrolyte for High-Rate and Low-Temperature Lithium Metal Battery[J]. *Advanced energy materials* 2022, 12 (42). <https://doi.org/10.1002/aenm.202200621>.
- [3] Zou, Y.; Cheng, F.; Lu, Y.; Xu, Y.; Fang, C.; Han, J. High Performance Low-Temperature Lithium Metal Batteries Enabled by Tailored Electrolyte Solvation Structure[J]. *Small* 2023, 19 (14). <https://doi.org/10.1002/smll.202203394>.
- [4] Gao, Y.; Rojas, T.; Wang, K.; Liu, S.; Wang, D.; Chen, T.; Wang, H.; Ngo, A. T.; Wang, D. Low-Temperature and High-Rate-Charging Lithium Metal Batteries Enabled by an Electrochemically Active Monolayer-Regulated Interface[J]. *Nature Energy* 2020, 5 (7), 534–542. <https://doi.org/10.1038/s41560-020-0640-7>.
- [5] Wang, Y.; Chen, Z.; Wu, Y.; Li, Y.; Yue, Z.; Chen, M. PVDF-HFP/PAN/PDA@LLZTO Composite Solid Electrolyte Enabling Reinforced Safety and Outstanding Low-Temperature Performance for Quasi-Solid-State Lithium Metal Batteries[J]. *ACS Applied Materials & Interfaces* 2023, 15 (17), 21526–21536. <https://doi.org/10.1021/acsami.3c02678>.

- [6] Zhang, D.; Zhu, D.; Guo, W.; Deng, C.; Xu, Q.; Li, H.; Min, Y. The Fluorine-Rich Electrolyte as an Interface Modifier to Stabilize Lithium Metal Battery at Ultra-Low Temperature[J]. *Advanced functional materials* 2022, 32 (23). <https://doi.org/10.1002/adfm.202112764>.
- [7] Thenuwara, A. C.; Shetty, P. P.; McDowell, M. T. Distinct Nanoscale Interphases and Morphology of Lithium Metal Electrodes Operating at Low Temperatures[J]. *Nano Letters* 2019, 19 (12), 8664–8672. <https://doi.org/10.1021/acs.nanolett.9b03330>.
- [8] Wang, D.; Lv, D.; Liu, H.; Yang, J.; Qian, Y.; Chen, Z. Forming Solid-Electrolyte Interphases with Rich Grain Boundaries on 3D Lithiophilic Skeleton for Low-Temperature Lithium Metal Batteries[J]. *Energy storage materials* 2022, 49, 454–462. <https://doi.org/10.1016/j.ensm.2022.04.020>.
- [9] Zheng, S.; Geng, H.; Eliseeva, S.; Wang, B.; Wu, Y.; Sen Copy; Fangling Production. Air-Exposed Lithium Metal as a Highly Stable Anode for Low-Temperature Energy Storage Applications[J]. *Energy materials* 2022, 2 (6), 200042–200042. <https://doi.org/10.20517/energymater.2022.66>.
- [10] Hong, L.; Ren, H.; Wang, Y.; Liu, Y.; Xiang, H. Designing on Solvent Composition of Dual-Salt Low Concentration Electrolyte for Inhibiting Lithium Dendrite Growth at $-20\text{ }^{\circ}\text{C}$ [J]. *Electrochimica acta* 2022, 414, 140238–140238. <https://doi.org/10.1016/j.electacta.2022.140238>.
- [11] Guo, C.; Guo, Y.; Tao, R.; Liao, X.; Du, K.; Zou, H.; Zhang, W.; Liang, J.; Wang, D.; Sun, X.-G.; Lu, S.-Y. Uniform Lithiophilic Layers in 3D Current Collectors Enable Ultrastable Solid Electrolyte Interphase for High-Performance Lithium Metal Batteries[J]. *Nano Energy* 2022, 96, 107121. <https://doi.org/10.1016/j.nanoen.2022.107121>.
- [12] Liu, H.; Cheng, X.; Yan, C.; Li, Z.; Zhao, C.; Xiang, R.; Yuan, H.; Huang, J.; Kuzmina, E.; Karaseva, E.; Kolosnitsyn, V.; Zhang, Q. A Perspective on Energy Chemistry of Low-Temperature Lithium Metal Batteries. *iEnergy* 2022, 1 (1), 72–81. <https://doi.org/10.23919/ien.2022.0003>.