

A review of low-temperature lithium metal battery research

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Abstract. Rechargeable lithium metal batteries (LMBs) are one of the promising energy storage systems, which have the advantage of a high theoretical specific capacity of 3860 mAh/g and a low reduction potential of -3.04 V vs. SHE. With the development of society, the large use of batteries in low-temperature areas is inevitable. Typically, batteries fail at low temperatures, especially with temperatures below -20 °C, but the research on low-temperature behavior is limited. According to previous research on low-temperature lithium metal batteries, the main challenge is to suppress serious dendrite growth at low temperatures. Here, we reviewed the state-of-art progress of low-temperature LMBs, including protect layer, three-dimensional collector, and electrolyte. We found that most of the research works relate to electrolytes because a novel electrolyte can easily solvate, contribute to ion transportation, and be conducive to solid electrolyte interfacial (SEI) film formation, which can accelerate the kinetics at low temperatures, thus suppressing the serious dendrite growth at low temperatures. We propose that solid electrolytes can suppress the dendrite growth of LMBs at low temperatures effectively because solid electrolytes are not easy to be pierced.

Keywords: Low temperature; lithium metal battery; lithium dendrite; electrolytes; solid electrolyte.

1. Introduction

Lithium metal has a high theoretical capability. What is more, it has the lowest discount plausible, and a low density of 0.534 g cm⁻³. Usually, using the super-high ability and special lithium storage mechanism of Li metal as an alternative to graphite can reduce capability loss in lithium-ion batteries (LIBs). When deciding on electric-powered transportation, electricity storage over a vast operational temperature varies is vital. But, regular Li-ion batteries endure extreme ability degradation beneath zero °C and mostly give up to function under -20 °C. Therefore, at low temperatures, it is unrealistic to employ LIBs. On the contrary, Li metal batteries (LMBs) function with the aid of plating/stripping with restrained solid-state diffusion; therefore, they may additionally be extra achievable for low-temperature applications.[1] However, when lithium is at low temperatures, the formation of lithium dendrites extremely reduces their applications under sub-zero. For example, at temperatures beneath -30 °C, Thenuwara et al have proven that carbonate-based electrolyte structures are no longer ample for LMBs operation, indeed with antifreeze sellers.[2] To remedy this problem, many efforts are dedicated to stabilizing the interface of SEI. Besides, suppressing dendrite growth is also a good way, such as floor safety layers, three-d hosts, synthetic SEIs, and electrolyte engineering.

Many scientists are developing novel electrolytes, efficient collectors, and protective layers to suppress the dendrite growth in low-concentration electrolytes.

This article mainly reviews the study of novel electrolytes at low temperatures to prevent the growth of dendrite in lithium metal batteries. It provides a feasible idea for enhancing the capacity of low-temperature lithium metal batteries after recycling (Fig.1).

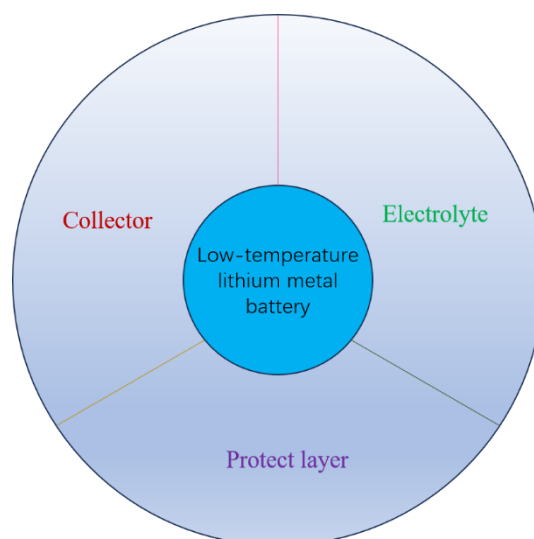


Fig 1. Overview chart.

2. Research progress of lithium metal batteries in low temperature

There are many ways to suppress lithium dendrite growth like developing novel electrolytes, researching 3D current collectors, and discovering new diaphragms. But, developing novel electrolytes is the most effective method. Herein, I reviewed the development of low-temperature lithium metal anode electrolytes.

2.1. Electrolyte

In DOL/DME-based electrolytes, Thenuwara et al study the SEI properties of Li metal electrodes at $-80\text{ }^{\circ}\text{C}$. According to cryogenic transmission electron microscopy (CTEM) and with the help of X-ray photoelectron spectroscopy (XPS) temperatures have a significant impact on the SEI's structure, chemistry, transport characters, with various inorganic phases being visible within the amorphous layer at a low temperature. These findings represent a significant advancement toward the creation of batteries with high energy that can function effectively over an extensive temperature scope.[2]

According to Thenuwara et al., adding fluoroethylene carbonate (FEC) to the solvent of the ether changes the SEI's chemistry and structure at a low temperature. The amplification in the related crystalline compounds part in the FEC-modified electrolyte machine is possibly recommended for biking manifestation. It is recorded that the FEC decomposition/reduction on Li metal surface contributes to the constitution of hydrocarbons, LiF and Li_2CO_3 , however, FEC is in particular employed as an additive to different carbonate solvents. In this part, the use of each CTEM and XPS, confirms that comparable decomposition reactions are going on indeed in the presence of ether solvents. So, FEC can be employed as a purposeful addition inside ether-based electrolytes to adjust the SEI, with unique advantages for biking the overall behaviour of anodes of LMBs in low-temperature environments.[1]

Zhang et al file an electrolyte with top-notch excessive present-day density and performance in low temperatures. In the electrolyte situation, it forms the thick and microstructural "Chain Link Ships" SEI. What is more, the components enhance the ester electrolytes' desolvation capability of Li^+ . In the wicked surroundings at $-30\text{ }^{\circ}\text{C}$, this common effectivity of the Li||copper battery achieved 98% even after cycling 200 times. Indeed, the Li||LiFePO₄ battery at $-40\text{ }^{\circ}\text{C}$ suggests 90% potential reservation after cycling one hundred times at the cathode-limited areal ability of 5 mAh cm^{-2} . Besides, Li||LFP full cells can cycle one thousand and two hundred times at a current of 5 C, and the capability retention rate is around 93.5% when it is at $-30\text{ }^{\circ}\text{C}$. The shaped bendy interface is known as "Chain Link Ships" SEI (Figure 2). This bendy SEI efficaciously reduces the increase of the lithium dendrite, adjusts the extent adjustments in the manner of lithium deposition, and decreases the ion switch barrier in the process of Li plating/stripping.[3]

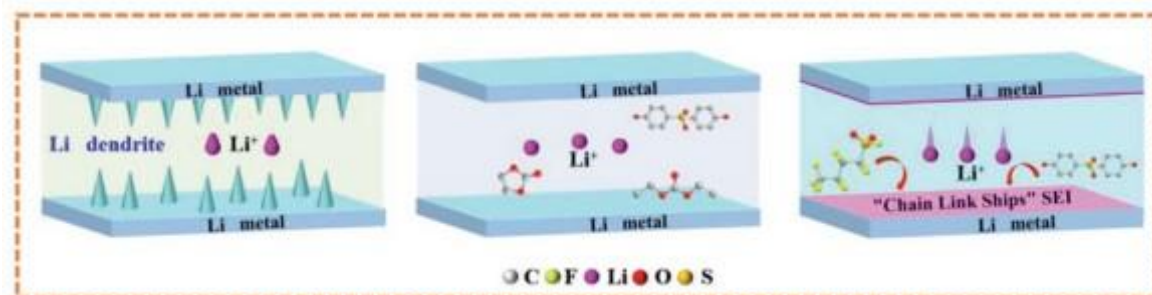


Fig. 2. Smoothing the lithium metal anode by modifying the electrolyte as an interface modifier. Chemical design between electrolyte interface and Li plate.

Xu et al rent a localized surprisingly focused electrolyte as a standard system. At subzero working temperature, it reports that the ionic attention gradient performs a main position in the polarisation of the cathodic Li electroplating method. A decoupling electrolyte plan approach is introduced to isochronously alleviate the kinetic polarization and construct a stable anion-derived SEI, for this reason, promoting an extraordinarily superior Coulombic effectivity of Li with a reduced telephone overpotential and a greater than three instances longer lifespan in realistic full cells at -20°C . [4]

At a low temperature, Liu et al discover an efficient electrolyte, which consists of the bis(fluorosulfonyl)imide anion (FSI)(EmimFSI) and 1-ethyl-3-methylimidazolium cation (Emim⁺), 1,2-difluorobenzene (dFBn), and LiFSI, the regular liquid electrolyte (ILE), i.e., [LiFSI]₁[EmimFSI]₂, are chosen as the mannequin electrolyte which is considered as the compatibility of LCILEs towards lithium metal anodes (LMAs) and they have an impact on of the non-solvating cosolvent. It is expected that the LMB using the regular ILE can't function well at the temperature of -20°C with a density of 0.1mA cm^{-2} . FEdF shows an entirely enhanced ionic transport, capacitating lithium stripping/plating at densities up to 0.5mA cm^{-2} benefiting from the properly kept Li⁺ solvation and structure. What is more, at -20°C , FEdF provides a high stripping/plating Coulombic efficiency (CE) of 98.3% and 1600h dendrite-free biking of Li/Li symmetrical cells, which outcomes additionally from the SEI prosperous in inorganic compounds. What is more, at -20°C , FEdF shows high compatibility with $\text{LiNi}_{0.8}\text{CO}_{0.15}\text{Al}_{0.05}\text{O}_2$ high-voltage cathode. At -20°C , by improvement of the electrolyte components, a high lithium strip ping/plating effectivity of 98.9% was done. [5]

Solid electrolytes have been studied very little, and this is the only solid electrolyte study in this review. Wang et al recommend a composite solid electrolyte render the PVDF-HFP/PAN/PDA@LLZTO-LiTFSI. The PDA@LLZTO had been once organized by way of an easy and environment-friendly technique to limit the floor electricity of sheer LLZTO and therefore gain the same solution. Adding PDA@LLZTO filler offers more advantageous ionic yields and conductivity and an excellent ion transference number, most likely as a result of the development of polymer-inorganic interactions acting as ion transport paths. Therefore, taking the gain of a blended polymer matrix and PDA@LLZTO filler, after modification the solid electrolyte further attains excessive mechanical resistance, favorable ionic conductivity, and the most desirable thermal stability. A very little amount of liquid electrolyte (4 L) used to be dumped at the interface when building cells to improve the interface wettability, as well as lower the battery operation temperature. The fabricated full cell attains excellent lithium stripping/plating stability for greater than two thousand hours, revealing significantly more advantageous price functionality and extraordinary long-term biking performance below 0°C . The cells also reveal good performance at low temperatures between -30 to -10°C . The cells can also operate safely when cutting, mechanical folding, and drilling are present, showcasing their high level of safety. [6]

Sun et al look up that a technique for manipulating anionic coordination is researched to substantially enhance the price capability of the electrolyte barring the employment of a high-concentration electrolyte. Especially, we display that, along with the necessary anion with a passable coordination skill, including a 2nd kind of anion with more desirable coordinating capacity than the solvent molecules can have the funds for an extra environment-friendly enlarge of t_+ , in contrast with the traditional treatment to extend the electrolyte concentration. The huge increase in t_+ would not

need an excessive number of coordinating anions in the solvation structure, which can significantly reduce energy dissipation by dragging anions. Due to the degraded anionic coordination manipulation, a high t_+ of 0.9 can be done while also influencing the conductivity of ions in the low-attention electrolyte (1 M). By similarly decreasing the populace of solvent molecules to 4M and weakening the interplay electricity of adjoining solvation complexes thru the addition of non-polar diluents, a multilayer solvation shape electrolyte is obtained, the components of the first, second, and third shells are shown in Scheme 1. Even in low-concentration electrolytes (1 mol L^{-1}), an excessive t_+ up to 0.9 can be achieved by managing the anionic species with outstanding coordination skills. High Coulombic effectivity of 99% can be obtained under a high cutting-edge density of 3 mA cm^{-2} , achieving enhanced performance in the high-loading pouch cells of LMB. This is accomplished by forming a multilayer solvation shape. This is achieved by using non-polar diluents. Furthermore, anodes at below-freezing temperatures and LMBs at zero degrees Celsius also exhibit excellent biking stability when using multilayer solvated shapes in electrolyte engineering (Fig.3).[7]

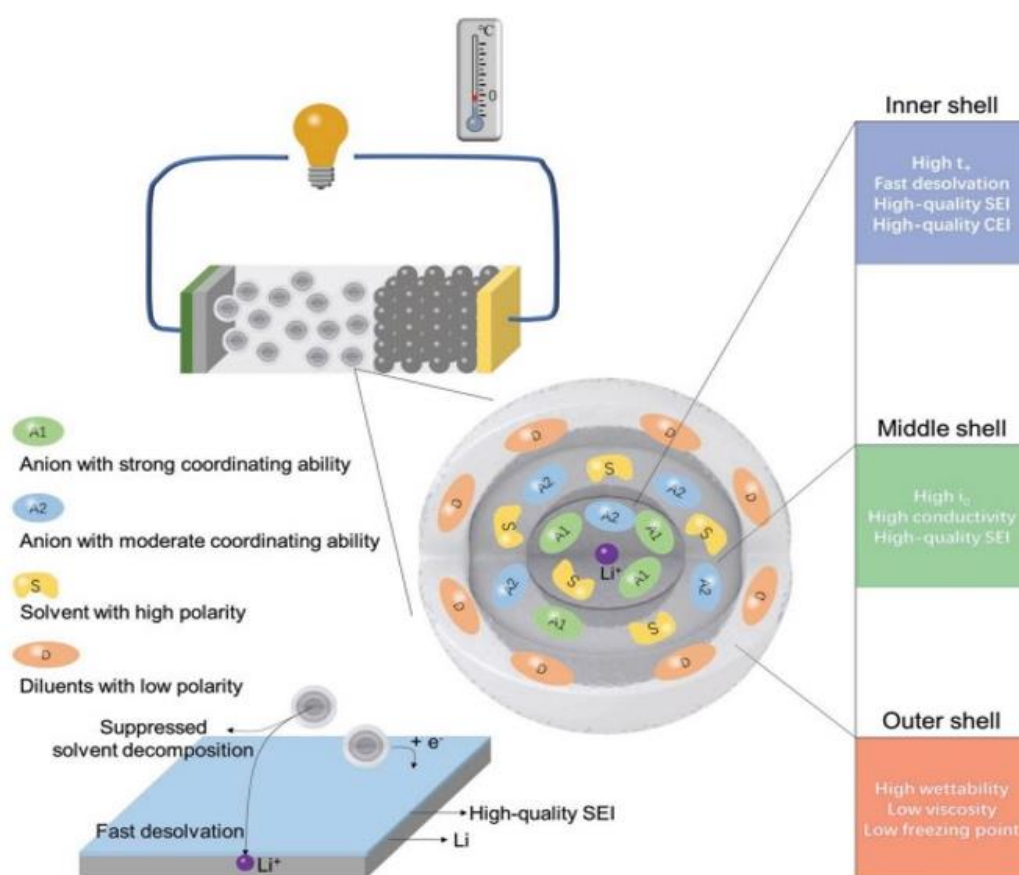


Fig 3. The multilayer solvation structure of LMB electrolytes for high and low-temperature application.

To investigate the effects of ion-pairing in the nearby solvation shape at low-temperature, Holoubek et al. designed a variety of high-concentration electrolytes. It used to be determined that solely structures with DME/ Li^+ molecular ratios of ≤ 2.4 had been successful in presenting reversible Li plating at the environment below -20°C . Additionally, it was noted that this performance pattern went against the ionic transfer data, which seemed to support the superiority of distantly unaware structures. With the help of MD data, it was once discovered that the overall behavior transition was once concurrent with a wonderful shift in Li^+ solvation shape where ion-pairing used to be a defining characteristic, and in basic terms solvent dominated environments had been owing to the lack of on-hand DME molecules. Previous studies have indicated that ion-pairing can affect the stability of the inner-sphere and the energies involved in outer-sphere reorganization. These effects are believed to be independent of temperature and can enhance performance at low temperatures. Finally, two additional Li||NMC 811 full cells had been assembled using electrolytes with excessive and low

nearby concentrations to demonstrate the effects of solvation during battery operation. The cells with electrolytes that have tremendous ion-pairing ability have shown the potential to maintain 63% of their room temperature power output after cycling for up to one hundred times, with minimal capacity degradation. At low temperatures, this work clearly shows that using ion-paired solvation can improve the reversibility of Li metal, this provides a feasible way for charging and discharging LMBs.[8]

Zou et al record that a novel electrolyte, which can be easily removed from the solvent and is favorable for interfacial movie formation, has been designed for lithium metallic batteries at low temperatures. Diethyl fluoromalonate, FEC, and fluorinated carbonate are used as solvents, while an excessive amount of LiTFSI. By the modification of the electrolyte composition, it is possible to decrease the bonding power between Li^+ and solvent molecules by promoting the mixing of lithium ions with anions in the excess-centered fluorinated carboxylic ester electrolyte. The application of the de-solvation technique at low temperatures is recommended. At $-30\text{ }^{\circ}\text{C}$, the electrolyte enables the Li | LiFePO_4 (LFP) cell to obtain a capacity of 91.9 mAh g^{-1} . At $0\text{ }^{\circ}\text{C}$, the capacity of Li | LFP cell retains over 100 mAh g^{-1} after 100 cycles, benefiting from the optimized desolvation kinetics.[9]

Zheng et al discovered that by designing low-concentration electrolytes with Li^+ -anion nanometric aggregates (LA-nAGG), they were able to accelerate the transportation of ions between the interface of electrolytes and the electrode. Instead of donor solvents, by coordinating Li^+ with TFSI $^-$ and fluorosulfonyl (FSI) $^-$ anions, which enable the formation of inorganic-rich interfacial layers and facilitate the movement of Li^+ . As a result, at $-70\text{ }^{\circ}\text{C}$, the ionic conductivity of LA-nAGG low-concentration electrolytes up to 0.6 mS cm^{-1} and the activation energy of charge transfer are as low as 38.24 kJ mol^{-1} . At $-60\text{ }^{\circ}\text{C}$, this enabled cells to retain approximately 83.1% of the room temperature capacity.[10]

2.2. Collector

Some studies have focused on designing collectors to suppress dendrite. Wang et al. report the formation of a highly conductive SEI layer on a 3D Ni-NiO current collector, which was composed predominantly of Li_2O and Ni. The SEI layer showed abundance in grain boundaries and enabled the enhanced stability and electrochemical performance of the cathode material. They discover that a 3D Ni-NiO current collector may be used to in-situ produce a grain-boundary-riched SEI film, which can dramatically improve Li^+ transportation at low temperatures. This porous, lithiophilic 3D hosts have a strong affinity for Li, which lowers the nucleation overpotential, leaves room for Li deposition, and effectively lowers local current densities for uniform charge distribution. The SEI layer exhibits low diffusion energy barriers for Li^+ at the grain boundaries between (111) facets of Li_2O and Ni, which makes it easier for Li^+ to pass through the interface. As a result, cells with the redesigned electrode have a high charge-discharge efficiency of 99.1% and a long life of 1600 hours. The 3D Ni-NiO current-collector-based Li||NCM811 cells exhibit outstanding cycling stability, after 160 cycles, even at a constrained Li supply and a high areal capacity circumstances the capacity retention rate is 80.8% after 160 cycles. When compared to non-lithiophilic 3D substrates, Li||NCM811 complete cells with the 3D Ni-NiO foam exhibit superior cycling stability with restricted Li anode (N/P = 1.2) and a substantial areal capacity of 3.2 mAh cm^{-2} . The 3D lithiophilic substrate's grain boundary-rich SEI layer has significant promise for producing high-efficiency, low-temperature LMBs. Despite some reported efforts to change the 3D hosts' user interface, their work demonstrates significant advancements for the practical Li metal anode, particularly for the Li metal batteries at low temperatures.[11]

At low temperatures, Gao et al record an interfacial manipulation strategy to help Li metallic anodes become stable. In this method, a self-assembled monolayer on copper collectors is designed to regulate the structure of SEI and nucleation of Li. By in situ forming lithium fluoride (LiF) nuclei on Li metal, this monolayer modifies the chemical environment of interfacial. As a result, the decomposition of electrolytes at the interface is altered, leading to the creation of a unique SEI with superior passivation and structural composition. Electrochemically active monolayer (EAM)

promotes Li nucleation and enhances its occurrence even at low interfacial Li ion concentrations by typing a lithiophilic anion, benzenesulfinate, onto Cu. At -15°C , a multilayered SEI is shaped that carries a LiF-rich internal section and an outer layer of amorphous material (Fig. 4). The SEI is special from the traditional SEI at low temperatures that shows a surprisingly crystalline and Li_2CO_3 -dominant structure. These points have been demonstrated using CTEM in tandem with scanning TEM and electron energy-loss spectroscopy, as well as high-resolution and depth-profiling XPS, and molecular dynamics simulation. To further clarify the main points, it is essential to provide a framework for the logical relationship between bits of information and between sentences. Specifically, what needs to be done is to offer more specific examples as evidence to support the experiment results, thereby avoiding any element of confusion and repetition. It is also necessary to proofread the paper thoroughly for grammar and spelling mistakes before submission. With the help of electrochemical atomic layer deposition (EAM-regulated SEI), we were able to achieve secure Li deposition across a temperature range of (-60°C to 45°C). This allowed us to successfully suppress the galvanic corrosion of Li anodes and self-discharge, resulting in a good $\text{Li}|\text{LiCoO}_2$ cell performance, which shows 200-cycle life under -15°C , high-capacity of 2.0mAh cm^{-2} , and high-rate charging (45 minutes). Between -15°C and 25°C , the batteries also exhibit stable reversible capacities [12].

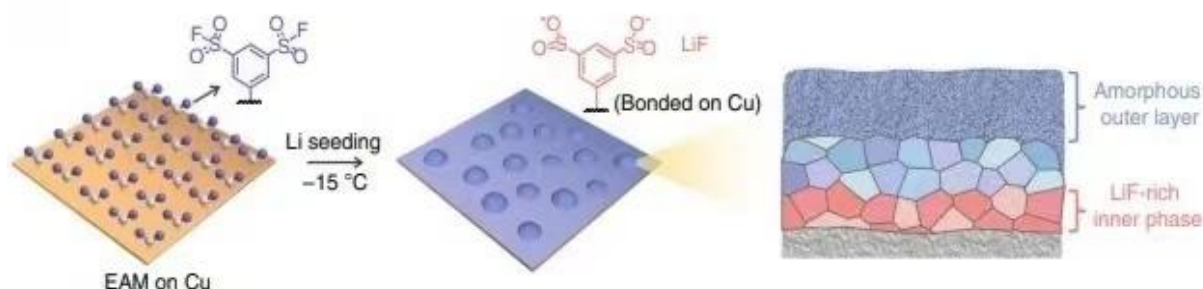


Fig 4. Li deposition on the EAM Cu with a uniform seeding of Li is achieved by forming a stable SEI layer.

2.3. Protect layer

Zhang et al discover that upon the addition of methyl butyrate (MB), a Li riched stable SEI is formed on the surface of lithium anode. Especially at low temperatures, this addition specifically promotes the desolvation of Li^+ at the interface (Fig. 5). In addition, when using MB as a co-solvent, the viscosity of the electrolyte decreased from 52.07 to $13.75\text{ mPa}\cdot\text{s}$. Meanwhile, at -20°C , the ionic conductivity increased from 1.38 to $3.44\text{ mS}\cdot\text{cm}^{-1}$. We further tested the $\text{Li}/\text{MXene}@$ liquid metal cells and found they could achieve a discharge potential of $500\text{ mAh}\cdot\text{g}^{-1}$ and retain 78% of their capacity after cycling 120 times at -20°C . [13]

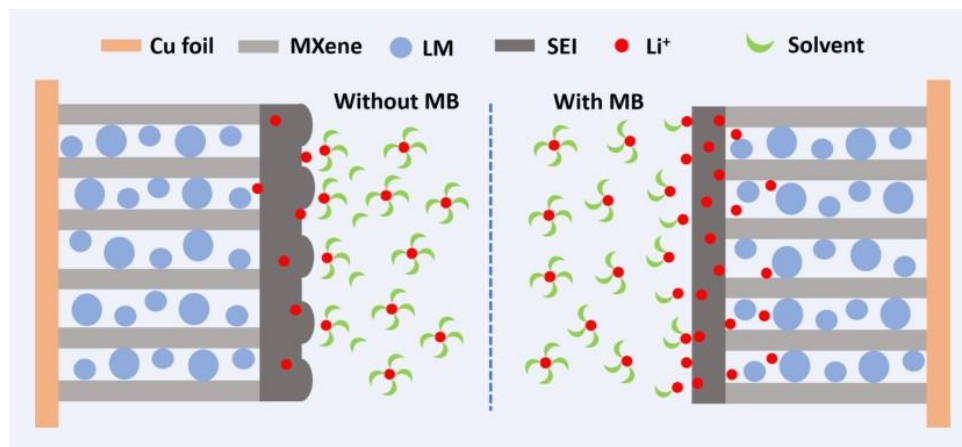


Fig 5. Comprehensive graphic content of LiF-rich (SEI) layer.

3. Conclusion

With the progress of science and technology, scientists will find more and more ways to suppress lithium dendrite growth. According to previous research, I find it is mainly the study of electrolytes to suppress lithium dendrite growth, finally improving the performance of the lithium metal battery. So, the study of electrolytes will also be one of the main research points in this area in the future mainly in SEI.

In recent years, with the continuous improvement of people's requirements for battery energy storage, lithium metal batteries are bound to attract the attention of scientists. Under low-temperature conditions, the working efficiency of the battery is one of the important conditions for testing the function of the battery. So far, research on low-temperature lithium-metal batteries has focused on the collector, electrolyte, and protection layer. The most important of these are electrolytes. However, there is not currently much research on low-temperature lithium metal batteries, and it is hoped that research in this area can be strengthened in the future.

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