

Strategies for electrolyte modification of lithium-ion batteries under low-temperature environments

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Abstract. Because of their high energy density, high voltage platform, extended cycle life, lack of memory effect, low self-discharge rate, environmental friendliness, and quick charging, lithium-ion batteries, or LIBs, are a vital component of contemporary electronic gadgets. Temperature has a complicated and wide-ranging effect on lithium-ion batteries, though. Lithium-ion batteries will have much-reduced performance, particularly in low-temperature conditions. The total performance of batteries is significantly impacted by the quality and performance of electrolytes in China. In particular, the electrolyte's purpose in lithium-ion batteries is primarily to convey lithium ions; the battery's ability to function at low temperatures is greatly influenced by the electrolyte's ion conductivity and SEI film-forming capabilities. Thus, this article begins by providing an overview of the fundamental composition and properties of lithium-ion batteries. The impact of low-temperature circumstances on lithium ion performance was then discussed. Lastly, many modification techniques were suggested from the electrolyte's point of view to enhance lithium-ion battery performance in low-temperature settings.

1 Introduction

People's need for energy is growing as science and technology advance, and finding effective ways to store and use energy has become crucial in today's world. Due to its effectiveness as a sustainable, eco-friendly, and renewable energy source, lithium-ion batteries are now a hot topic for study.

Lithium ions are moved between positive and negative electrodes in LIBs, which are a type of chemical battery that absorbs and releases electrical energy. It has been widely utilized in mobile communication devices, electric cars, energy storage devices, and other industries. Its characteristics include compact size, low weight, high energy density, and extended storage duration [1].

However, lithium-ion batteries have several significant drawbacks in low-temperature environments, which limit their application in cold conditions. First, the charging and discharging rates of lithium-ion batteries are significantly reduced in low temperatures, which not only affects the normal use of the batteries, but also may lead to a long charging time, or even the inability to be fully charged. Secondly, low temperatures will also cause the internal resistance of lithium-ion batteries to increase, which means that the battery in the working process will produce more heat, which not only reduces the energy conversion efficiency of the battery but also may cause safety problems. Furthermore, lithium-ion batteries' longevity will be impacted by a large decrease in their energy density at low temperatures. Lithium-ion battery service life may be shortened by prolonged usage

of the battery at low temperatures due to irreversible internal damage [2].

The majority of these have to do with how well the electrolyte performs. The electrolyte transfers lithium ions in lithium-ion batteries, and the battery's ability to function at low temperatures is greatly influenced by its ionic conductivity and SEI film-forming qualities. Thus, the major focus of this study is to describe the methodologies for electrolyte modification for lithium-ion batteries in low-temperature environments.

2 The impact of low temperature on lithium-ion batteries

2.1. Structure and mechanism

The lithium-ion battery mainly consists of three main components: the cathode, the anode, and the electrolyte, as shown in Fig. 1 [3]. The choice of lithium metal as the primary material for the anode is primarily because lithium is the lightest metal, and it possesses a very high specific capacity and a low electrode potential. However, the reactivity of lithium metal is too strong, which can easily lead to short circuits in the circuit. Researchers have designed special electrodes that insert lithium ions into graphite interlayers to limit the volume expansion of lithium metal during reactions and the growth of lithium dendrites.

In terms of cathode materials, scientists initially considered conversion-type cathode materials such as sulfides, but these materials can cause the electrode to

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undergo multiple cycles. Due to the limitations of such materials, researchers have designed metal sulfides with layered structures and storage spaces as a new direction for lithium-ion battery materials, such as the use of titanium disulfide. Although its energy density is limited, three commonly used oxide cathode materials were later discovered: lithium cobalt oxide (LiCoO_2), spinel LiMn_2O_4 , and polyanionic oxide $\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$ ($\text{X} = \text{S}, \text{Mo}, \text{W}, \text{etc.}$) [4].

It can be observed that layered oxides with high weight and volume energy density would be one of the most suitable cathode materials, but this does not affect LiCoO_2 's dominant position in the electronic device market. Lithium-ion batteries mainly involve redox reactions and the movement of lithium ions [5].

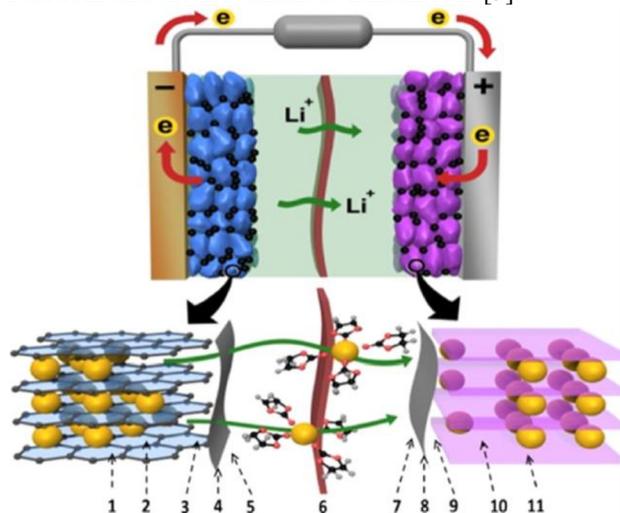


Fig. 1. The basic structure of LIBs [3].

2.2. The influence of LIBs in low-temperature environments

The fossil fuel crisis and environmental contamination have been major drivers of the electric car industry's growth. Due to their poor energy density and limited theoretical capacity, lead-acid and alkaline batteries are unable to keep up with the electric vehicle industry's continuously increasing needs. Due to its many benefits, lithium-ion batteries have drawn interest from scientists and entrepreneurs. They are now extensively utilized in nearly all electronic products as well as electric cars because of their high cycle performance and self-discharge characteristics. Nevertheless, the discharge voltage and capacity of lithium-ion batteries decrease dramatically below 0 degrees Celsius. Reduced driving range for electric cars might result from winter temperatures below -30 degrees Celsius in certain high-latitude countries, including Russia and Canada. Temperatures on Mars can dip below -130 degrees Celsius on winter nights, which means that to increase the spectrum of applications for lithium-ion batteries, their low-temperature performance needs to be improved [6].

2.2.1 Decreasing ion conductivity of the electrolyte

The capacity of ions to conduct inside an electrolyte is referred to as conductivity, and it is frequently used to assess the rate of ion transit throughout the electrolyte in a battery. The electrolyte's ion conductivity is a critical factor in the energy density and overall performance of lithium-ion batteries. The capacity of ions to flow through an electrolyte when subjected to an electric field is known as ion conductivity.

Ion mobility is reduced and ion conductivity is subsequently reduced as temperature drops due to an increase in the electrolyte's viscosity. In conclusion, low-viscosity electrolyte materials will show better ion conductivity at low temperatures. On the other hand, the dielectric constants of most low-viscosity solvents are low. The physical property known as the dielectric constant indicates a substance's polarization potential and the electrolyte solvent's capacity to separate lithium salt ions.

In electrolytes, the dielectric constant is an important parameter that directly affects ion movement in an electric field and the interactions between ions. Generally, solvents with high dielectric constants are better at dissociating lithium salt ions, promoting ion conduction, and exhibiting higher ion conductivity. However, strong intermolecular interactions in high dielectric constant solvents also mean that they have higher viscosity, such as cyclic carbonates and sulfonyl solvents, which may limit ion mobility and affect the functionality of the electrolyte.

Therefore, to achieve optimal ion conductivity, a balance between viscosity and dielectric constant is required, necessitating solvent combinations in the electrolyte that possess low viscosity and high dielectric constant [7].

2.2.2 Sluggish charge transfer process

Lithium battery discharging capacity will be limited at low temperatures due to a decrease in charge transfer capability between the electrolyte and electrode, in addition to electrolyte conductivity. In lithium-ion batteries, charge transfer normally occurs in four stages. First, at the electrolyte's outer Helmholtz plane, solvent coordination with lithium ions is seen. Subsequently, solvent coordination removes big solvent molecules from this plane. Lithium ions, anions, and a few tiny neutral molecules are then selectively adsorbed onto the electrode surface's inner Helmholtz layer. Ultimately, solvated lithium ions embed in electrode materials, conduct redox reactions, and diffuse across the organic and inorganic layers of the SEI membrane in various diffusion modes. Charge transfer impedance is used to assess charge transfer during charging and discharging periods; an increase in its value causes a delay in the responses associated with charge transfer. Lithium-ion resistance is primarily affected by charge transfer impedance, which increases quickly with decreasing temperature. Numerous elements, including dissolution sheath structure, electrode voltage, and SEI, affect charge transfer impedance [8].

The temperature and process activation energy of charge transfer define the charge transfer impedance. To enhance LIBs' low-temperature performance, researchers are focused on lowering the activation energy of charge transfer processes. Research has indicated that the desolvation process of Li^+ and the binding energy of Li^+ at the electrode's surface sites determine the activation energy of the charge transfer process. To lower the binding energy and charge transfer impedance, many researchers are committed to enhancing the electrode surface.

2.2.3 Formation of lithium dendrites

Lithium-ion diffusion slows down when the working temperature drops, which causes dendrites to develop that are harmful to battery charging and discharging. These lithium dendrites can continually consume lithium ions and result in an unstable SEI interface. Lithium dendrite formation is aided by the decrease in the maximum concentration of Li^+ and the diffusion coefficient of Li^+ in the SEI at low temperatures. High SEI resistance and low Coulombic efficiency come from lithium dendrites growing on the lithium metal anode penetrating the separator, generating a short circuit in the battery and encouraging the formation of new SEI to cover the lithium dendrites [9]. Figure 2 shows a photo of the formation of lithium dendrites.

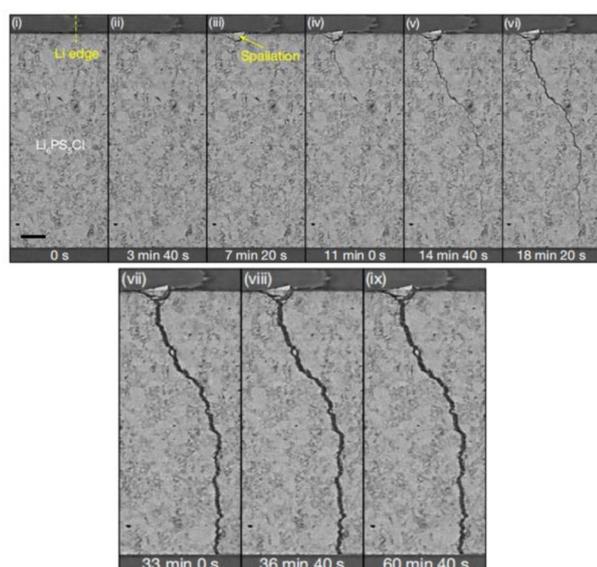


Fig. 2. Photo of lithium dendrite formation [9].

3 The impact of low temperature on lithium-ion batteries

3.1 Optimize solvent composition

Under low-temperature conditions, the performance of lithium-ion batteries tends to degrade, primarily due to changes in solvent viscosity and electrode repulsion reactions. To ensure stable charging and discharging capacities of lithium-ion batteries even in extreme environments, electrolyte solvents need to possess

characteristics of low viscosity and high dielectric constants. Additionally, it is necessary to design electrolyte solvents with good electrochemical stability and a wide liquid phase range [10].

3.1.1 Carboxylate salt

Carboxylate esters are excellent choices for low-temperature solvents because they retain their low viscosity and low freezing point properties at low temperatures. Nonetheless, carboxylate esters have a smaller electrochemical window and more volatility than carbonate esters. Scholars have devised many approaches to address the limitations while capitalizing on the benefits of ester solvents. Blends with their structural optimization being one of the easiest approaches. varied ester solvent mixtures have varied effects on battery performance [11].

Esters include both cyclic lactones and linear esters. Gamma-butyrolactone (GBL) is one of the cyclic lactones that has been studied the most. It has significant characteristics like low viscosity and low melting point. It allows for the effective ionization of lithium salts despite its lower dielectric constant. On the other hand, it has the same disadvantage as other esters in that it cannot effectively build a passivating layer on the anode. Researchers have combined LiBOB and GBL in a unique way to create batteries that operate better at low temperatures.

At low temperatures, aliphatic ester co-solvents can increase the ion conductivity of electrolyte solutions; nevertheless, conductivity diminishes as chain length increases. High molecular weight ester co-solvents or long-chain electrolytes can improve lithium-graphite batteries' low-temperature performance.

3.1.2 Carbonate

Lithium-ion batteries are a significant use for carbonate solvents. There are two types of carbonates: cyclic carbonates with a high dielectric constant and linear carbonates with low viscosity. High conductivity and the creation of a stable solid electrolyte interface (SEI) are two benefits of carbonate solvents. Among these are cyclic carbonates like PC and EC, and linear carbonates like DMC, EMC, and diethyl carbonate (DEC). Although EC is one of the most widely utilized carbonate solvents, its temperature range of use is insufficient. Researchers have discovered that EC single-solvent solutions are less conductive than multi-component solvent systems that contain both linear and cyclic carbonates. Additionally, PC has attracted attention as a solvent because of its wide liquid range and lower viscosity, which can improve low-temperature performance. Furthermore, sulfite and sulfate salts, due to their low melting temperature and low viscosity, can serve as good co-solvents to enhance low-temperature performance.

3.2 Additives

By altering the electrode-electrolyte contact, additives improve the electrolytes' overall performance. They can help reduce the composition of the SEI that is harmful to conductivity while creating a strong, highly conductivity solid electrolyte interphase (SEI). Additives are usually found in the electrolyte at a maximum mass fraction of five percent. Additives such as sulfur compounds, silicon-containing compounds, phosphorus-containing compounds, and fluorine-containing compounds can all help batteries function better under low-temperature conditions.

3.2.1 Inorganic lithium salt additives

The usage of lithium-ion batteries in low-temperature settings can be made safer and more effective with the help of inorganic lithium salt additions. The anode and cathode's surface conditions and solubility are improved by these additives, which increases the working temperature range of lithium-ion batteries. LiDFBOP, or lithium difluoro bis (oxalate)phosphate, is a common inorganic salt additive for lithium. Its complementary actions with the electrolyte can increase the battery's ability to discharge while encouraging the cathode's stable SEI layer to develop. It can also lessen the transition metals' dissolution from the cathode. The primary source of the passivation effect in batteries is thought to be the dimer created by the recombination of acyl radicals produced by the oxidation of anions on the surface of transition metal oxides. Lithium fluorophosphate is another structured inorganic lithium salt additive that is comparable. Using this additive can lower the electrode surface's resistance and create a stable SEI layer. This addition lessens structural deterioration and electrolyte oxidation by accumulating more inorganic lithium salt material on the cathode surface of batteries that include it.

3.2.2 Siloxane additive

Siloxane additives are considered to address the performance decline of lithium-ion batteries in low-temperature environments. Siloxane additives possess excellent ionic conductivity and stability. Hydroxyl groups interact with silica to form a gel, and the porous network structure of the gel can facilitate the flow of lithium ions in the electrolyte medium. However, hydroxyl groups can also interact with electrolyte components, potentially affecting the cycle life and performance of lithium-ion batteries. To address this issue, researchers have proposed a dual-additive approach of simultaneously adding lithium silicate nanoscale and PDMS-A. With this approach, lithium-ion batteries exhibit higher capacity in low-temperature environments compared to batteries without additives.

3.2.3 Organic electrolyte additives

The promise of organic electrolyte additives to enhance lithium-ion batteries' low-temperature performance has led to a great deal of research in this area. Organic sulfur

compounds are frequently found among them. These substances can lessen the effect of low temperatures on battery impedance because they have different structures and oxidation states. Furthermore, these organic electrolyte catalysts aid in the development of the SEI layer on the electrode surface, which is essential to the lithium-ion batteries' ability to operate as a charge-discharge system. It has been discovered by researchers that the reduction products of DMS and DTD help to improve the performance of lithium-ion batteries at low temperatures. Another popular issue is the use of organophosphates as electrolyte additives in lithium-ion batteries. They have several uses, including improving high-voltage stability and decreasing flammability. TMSP is a suggested addition that improves battery performance by preventing lithium dendrite formation and fortifying the stability of the cathode-electrolyte layer. Furthermore, adding even a tiny quantity of TMSP can boost battery performance in low-temperature conditions in ways that are not anticipated. Vinylene carbonate (VC) is one of the most common additives nowadays, capable of improving the morphology of lithium metal deposition and increasing the stability of batteries during cycling. The use of VC additives can make the lithium deposition layer denser, reduce cathode resistance under low-temperature conditions, and enhance battery function in harsh environments [11].

3.3 New Electrolyte Salts for Low-Temperature Lithium-Ion Batteries

3.3.1 Liquefied gas electrolyte

Fluorinated alkanes have garnered attention due to their favorable performance across a wide temperature range. Researchers utilize the vapor pressure within batteries to keep these fluorinated hydrocarbons, which are typically gaseous at room temperature, in a liquid state, thereby ensuring high conductivity and low viscosity. Additionally, the addition of co-solvents such as acetonitrile increases the solubility of lithium salts in liquefied gas electrolytes, mitigating the conductivity decrease caused by crystallization. Currently, researchers have experimented with using difluoromethane as an electrolyte in battery production, although addressing its flammability remains a concern.

3.3.2 Locally high concentrated electrolyte

The better oxidation stability, thermal stability, reduced side effects, and higher lithium ion transference numbers of high-concentration electrolytes are offset by increased electrolyte viscosity and decreased conductivity in lithium-ion batteries. Researchers have suggested designing regionally high-concentration electrolytes to enable lithium-ion batteries to operate normally in low-temperature conditions. In this design, the high-concentration electrolyte is mixed with a specific amount of non-polar diluents. Diluents are incapable of chemically interacting with lithium salts and solvents

because they often have low dielectric constants and weak electron-donating capacities. Because LiFSI and LiTFSI may inhibit the formation of lithium dendrites at high concentrations, they are currently widely utilized lithium salt compounds in locally high-concentration electrolytes. The most widely used diluent has a larger voltage tolerance because of the action of fluorine atoms, which makes it fluorinated ether.

3.3.3 Polymer electrolytes

Polymer electrolytes can still perform well in low-temperature environments. Researchers achieve good conductivity of the electrolyte at lower temperatures by adjusting the proportions of different polymer electrolytes in the mixture and adding a certain amount of additives. Succinonitrile can serve as an additive for polymer electrolytes, enhancing their conductivity and ability to dissolve lithium salts, thereby improving the electrolyte's cycling performance. Polymer electrolytes are highly flexible and lightweight, but their performance at low temperatures is relatively lower compared to liquid electrolytes [12].

4 Conclusion

Lithium-ion batteries offer several significant advantages that make them an indispensable power solution in modern electronic devices. This paper summarizes the effects of low-temperature environments on lithium-ion batteries, including reduced charge/discharge rates, reduced example conductivity, and the generation of lithium dendrites. To address these issues, this paper proposes three modification strategies based on the electrolyte perspective, including optimization of solvent composition, introduction of additives, and development of new electrolyte salts.

However, in low-temperature circumstances, the anode of lithium-ion batteries is also susceptible to lithium precipitation. The precipitated lithium reacts with the electrolyte, affecting the battery's performance and perhaps posing a safety risk. Thus, one key area of research for low-temperature lithium-ion batteries is the creation of anode materials that are more stable at low temperatures. Second, the battery's cycle life may be lowered by charging and discharging at low temperatures, which could cause an irreversible loss of capacity. Therefore, how to extend the cycle life of low-temperature lithium-ion batteries is also an urgent problem. Most importantly, low-temperature environments may increase the risk of thermal runaway in batteries, and effective safety measures are needed to ensure stable battery operation at low temperatures. This includes improving the structural design of the battery, optimizing the thermal management system, and improving the thermal stability of the battery. The development and production of low-temperature lithium-ion batteries usually requires the use of special materials and processes, which may increase production costs. Therefore, it is also an important challenge to reduce the production cost and achieve the commercialization of

low-temperature lithium-ion batteries while ensuring performance. To overcome these challenges, researchers are required to continuously conduct in-depth studies to explore new materials and processes and optimize the structure and design of the batteries, to improve the performance and safety of low-temperature lithium-ion batteries, and to promote their application and development in various fields.

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