

# *Research Progress of Lithium-ion Battery Electrolyte*

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**Abstract.** Research on the electrolyte of lithium-ion batteries can enhance battery performance, reduce production costs, and make battery application scenarios more extensive. At the same time, better electrolytes can promote the development of industries, such as the new energy industry and the chemical industry, enabling batteries to provide more convenience for human society and offer more benefits to the development of science and technology. However, the current electrolytes still have significant drawbacks, such as poor stability at high voltages, flammability and volatility. This has led to lithium-ion batteries being prone to explosion and combustion accidents, with insufficient safety and stability, and their application environments being relatively limited. This article focuses on enhancing the properties of electrolytes from three aspects: solution, electrolyte, and additive. Summarized ether and sulfone solutions; LiPF<sub>6</sub>, LiFSI and LiDFOB substances are mixed as electrolytes. The advantages and disadvantages of film-forming additives and flame-retardant additives in improving the performance of electrolytes. It has reference significance for the application of electrolyte components under different conditions.

**Keywords:** Lithium-ion battery electrolyte, Electrolyte additives, Flame-retardant properties

## 1. Introduction

In recent years, the number of new energy electric vehicles mainly powered by lithium-ion batteries has been increasing and improving. However, at the same time, many shortcomings of lithium-ion batteries have also emerged, such as short range, high cost, flammability and explosiveness, etc. Among them, the performance of lithium-ion batteries is mainly affected by the electrolyte. The ionic conductivity of the electrolyte is the key to the migration of lithium ions. When the conductivity is low, the charging and discharging speed of the battery will also slow down. The stability of the electrolyte determines the cycle life of the battery. If the stability is poor, the electrolyte will decompose on the electrode surface, generating impurities or eroding the positive electrode material, which will cause the battery capacity to decline rapidly. The safety of the electrolyte is even more crucial to the safety of the battery. Traditional organic electrolytes are flammable and volatile, and are more prone to safety accidents in the event of short circuits or overcharging. In addition, the physical properties of the electrolyte can affect the battery's adaptability to high and low temperatures. For instance, at low temperatures, the viscosity of the electrolyte increases, making ion migration difficult. At high temperatures, the evaporation or

decomposition of the electrolyte accelerates the aging of the electrodes. Therefore, the safety and stability of lithium-ion batteries can be enhanced by improving the composition of the electrolyte.

Traditional electrolytes mostly use organic solvents such as phosphate esters, which are flammable and volatile, prone to decomposition and gas generation at high temperatures, and can easily cause safety accidents. At the same time, it has poor performance at both high and low temperatures. At low temperatures, the viscosity of the electrolyte increases significantly, making battery charging and discharging difficult. At high temperatures, the stability of the electrolyte decreases, shortening the battery's cycle life. With the wide application of high-voltage cathode materials at present, traditional electrolytes are prone to oxidation and decomposition at high voltages, causing rapid decline in battery capacity. Traditional electrolytes have strict requirements for the production environment, and thus often require considerable costs. In response to the defects mentioned above, currently, improvements can be made to the solvents, electrolytes and additives in the electrolyte. For instance, ethers and sulfones can be used as solvents to enhance performance. Mix  $\text{LiPF}_6$ , LiFSI and LiDFOB substances as electrolytes; Introducing additives into the electrolyte, such as using film-forming additives, can inhibit the decomposition of the electrolyte.

This article focuses on enhancing the properties of electrolytes from three aspects: solutions, electrolytes, and additives, and summarizes ether and sulfone solutions.  $\text{LiPF}_6$ , LiFSI and LiDFOB substances are mixed as electrolytes. The advantages and disadvantages of film-forming additives and flame-retardant additives in improving the performance of electrolytes aim to optimize the composition of electrolytes and enhance the stability and safety of lithium-ion batteries.

## 2. Lithium-ion battery electrolyte

The electrolyte of lithium-ion batteries mainly consists of three parts: solvent, electrolyte (solute) and a small number of additives. Firstly, solvents, as carriers for ion migration, possess high dielectric constants and low viscosity. Secondly, the solutes present in the electrolyte of lithium-ion batteries are often electrolytes, which can provide lithium ions and ensure charge conduction. Finally, to optimize the performance of lithium-ion batteries, a small number of additives are often added to the electrolyte. The three parts complement each other to maintain battery performance and ensure its stability and safety.

### 2.1. Solvent

In the electrolyte of lithium-ion batteries, solvents are the core components and mainly have the following functions. Dissolving the electrolyte and dissociating lithium ions from lithium salts to allow them to move freely provides the electrolyte with the ability to conduct electricity. To maintain ion mobility, solvents can influence the mobility of ions through their own dielectric constant and viscosity, thereby affecting the battery. Stabilizing the electrode interface, the solvent can form a stable SEI film through interaction with the electrode material, protecting the electrode. At present, the main types of solvents are phosphate esters, ethers, carboxylate esters, sulfones and nitriles. Among them, phosphate esters are currently the most widely used, and in practical applications, the solvents are often in a mixed form.

### 2.2. Solute

In the electrolyte of lithium-ion batteries, the solute (electrolyte) is used to provide conductive ions, and its core functions have three aspects. Provide conductive ions to offer basic conductivity to the

battery. Lithium ions directly participate in electrode reactions during charging and discharging. Some electrolytes will react with the electrodes to form a stable SEI film. The main types of electrolytes include hexafluorophosphate, tetrafluoroborate, bis (fluorosulfonyl) imide, and bis (trifluoromethylsulfonyl) imide. Among them, hexafluorophosphate has balanced performance and is currently the most widely used.

### 2.3. Additive

Introducing additives into the electrolyte of lithium-ion batteries can significantly improve the electrolyte and enhance battery performance. Additives can improve the stability of the SEI film, enhance the safety of the battery, optimize the electrochemical performance of the battery, inhibit side reactions and protect the structure of electrode materials. To better optimize the comprehensive performance of batteries, additives are often used in a compound form. Among them, film-forming additives are the most commonly used category. Flame-retardant additives reduce the flammability of the electrolyte and enhance battery safety. Overcharge protection additives form an insulating layer to block the current and protect the battery when it is overcharged. Conductive additives are used at low temperatures to improve the ion migration efficiency in the electrolyte. Metal ion chelating agents can reduce the damage of transition metal ions to the SEI film. In conclusion, appropriate additives can be selected and compounded based on different application scenarios and conditions.

## 3. Modification

To optimize the performance of batteries, it is necessary to enhance the electrochemical performance of the electrolyte, increase its stability and safety. As the core material in lithium-ion batteries, the electrolyte plays a role in conducting lithium ions, stabilizing the electrode interface, and maintaining the overall chemical environment of the battery. To increase the upper limit of energy storage of the battery, extend its cycle life, and expand its operating temperature range. It can be implemented through three aspects: changing the solution, solute and introducing additives.

### 3.1. Solvent modification - ether and sulfone solvents

As the base of the electrolyte, the physical and chemical properties of the solvent will directly affect the migration rate of lithium ions in the electrolyte, the stability of the electrode interface and the safety and stability of the battery. Research shows that the heat release from the decomposition reaction of the electrolyte is related to the lithium salt solvent [1]. Therefore, by mixing different solvents, the conductivity and stability of lithium-ion batteries can be enhanced.

Among them, organic solvents belonging to ethers and sulfones can significantly improve the performance of the electrolyte. Ether solvents, due to the presence of flexible ether bonds in their molecular structure, have a relatively low viscosity at low temperatures, ensuring that lithium ions still have a high migration speed in low-temperature environments. This enables lithium-ion batteries to maintain good charging and discharging performance under low-temperature conditions. The flexible characteristics of its molecular chain reduce the intermolecular forces, so that the performance of the solvent will not be significantly affected even in low-temperature environments. Meanwhile, ether solvents have excellent interfacial compatibility with lithium metal electrodes and can form a stable interfacial film, providing a stable environment for the precipitation and dissolution of lithium and enhancing the safety of lithium-ion batteries. Lithium metal, as a high-

capacity anode material, its lithium dendrite growth can lead to interface instability. However, ether solvents can form a dense, uniform SEI film with high lithium-ion conductivity on the electrode surface, which can effectively suppress the safety risks brought by lithium dendrites and increase the cycle life of lithium ions. However, the safety shortcomings of ether solvents cannot be ignored either. They often have the characteristics of low boiling point, high volatility at high temperatures, poor thermal stability and flammability, which make them pose a significant safety hazard in high-temperature environments.

The molecular structure of sulfone solvents contains highly polar sulfone groups. Due to their stability, sulfone solvents have high boiling points and flash points, and are less likely to volatilize and burn in high-temperature environments. They can effectively enhance the thermal stability of lithium-ion batteries, delay the process of battery thermal runaway, and improve the safety and stability of batteries in high-temperature environments. Strong polarity also endows sulfone solvents with a relatively high dielectric constant, which can promote the dissociation of lithium salts, reduce free solvent molecules, slow down the process of solvent oxidation and decomposition, and enhance the flame retardant performance of the electrolyte. However, due to the high viscosity of sulfone solvents, the fluidity of such solvents will further decline in low-temperature environments, causing a sharp drop in the capacity of batteries at low temperatures and significantly deteriorating the performance of lithium-ion batteries at low temperatures.

There are two main types of substances in ether organic solvents: cyclic ethers and chain ethers. Research shows that cyclic ether is the electrolyte with the best performance known, and its electrical conductivity is much higher than that of other binary mixed solvent electrolyte systems. Adding a certain amount of DME, which belongs to chain ethers, to the organic electrolyte can also increase the conductivity, but at the same time, its strong reactivity will make the SEI film formed with lithium unstable [2]. Research shows that by using electron-absorbing sulfone groups, such as TMS, Panasonic has mixed them with fluorinated ethers and used lithium diimide (LiBETI) as lithium salts, enabling the electrolyte to maintain good performance and high charging efficiency under high temperature and high pressure [3].

In conclusion, to ensure the safety of batteries in both low-temperature and high-temperature environments, ether-sulfone compound solvents have become the mainstream choice in the industry. By introducing an appropriate amount of low-viscosity ether solvents, the viscosity of the solvents can be reduced while maintaining the high stability of sulfone solvents. For different application environments, different compounding ratios should be used. For instance, in cold environments, the proportion of ethers should be increased to enhance low-temperature conductivity, while in high-temperature environments, the proportion of sulfones should be raised to strengthen safety.

### 3.2. Solute modification-LiPF<sub>6</sub>, LiFSI, and LiDFOB substances are mixed as electrolytes

As the core medium for conducting charges in the electrolyte, the electrolyte can dissolve the solute and dissociate lithium ions, ensuring the normal operation of the battery. Secondly, the electrolyte also provides a suitable ionic environment for the oxidation-reduction of the positive and negative electrodes of lithium-ion batteries, enabling the battery to achieve the energy conversion between chemical energy and electrical energy. However, at the same time, the conductivity and stability of the electrolyte also directly affect the charging and discharging rate of the battery, as well as its cycle life and safety. Therefore, mixing different electrolytes can improve the performance of batteries to a certain extent. Research shows that the best electrolyte salt for lithium-ion batteries at present is LiPF<sub>6</sub>, which is widely used in various types of lithium-ion batteries and can form a stable SEI film at the electrode/electrolyte interface. However, its disadvantages are also obvious, such as difficulty

in production, poor thermal stability, poor storage conditions, and high cost [2]. Studies show that LiFSI has better performance than  $\text{LiPF}_6$ . It has good low-temperature rate performance and will not corrode the positive aluminum foil [4]. Research shows that the interfacial film formed by LiDFOB is more stable, has a lower impedance and can reduce the oxidation polymerization of EC in the electrolyte [5]. In conclusion, the mixed use of these three substances as electrolytes based on different application conditions can comprehensively enhance multiple performance aspects of lithium-ion batteries as required.  $\text{LiPF}_6$  has high electrical conductivity, LiFSI can increase the number of lithium-ion migrations in the electrolyte, and LiDFOB can provide high electrical conductivity at both high and low temperatures. LiFSI can prevent the positive electrode aluminum foil from being corroded, and LiDFOB can form a stable SEI film, enhancing stability at high voltages. Therefore, the mixed use of the three can keep the electrolyte stable at high voltages.

### 3.3. Additive

Although additives account for a very small proportion in the electrolyte, they can precisely optimize the SEI film through selective reactions or physical actions, thereby enhancing the safety of the electrolyte [6]. At present, the mainstream additives can be divided into two types: film-forming additives and flame-retardant additives, which can regulate the stability and safety of the battery interface.

#### 3.3.1. Film-forming additive

Film-forming additives can preferentially undergo REDOX reactions on the surface of lithium-ion battery electrodes, forming a stable SEI film, thereby reducing losses, lowering the risk of internal short circuits, thermal runaway and other safety issues in the battery, and enhancing the battery's cycle life. Studies have shown that both vinylidene carbonate (VC) and vinyl carbonate (VEC), which are currently widely studied, can improve the performance of lithium-ion batteries due to their unsaturated double bond energy, which preferentially decomposes over PC during electrochemical processes [7]. The introduction of additive VC can form a dense CEI film on the surface of the cathode material, thereby suppressing the interfacial reaction between the electrolyte and the cathode material and improving the low-temperature electrochemical performance of lithium batteries [8]. When the two are combined, VC has a faster film-forming speed, while VEC has good chemical stability, which enhances the performance of the SEI film. VC can improve the low-temperature charge and discharge efficiency of batteries, and VEC can enhance chemical stability, enabling batteries to have better performance over a wider range of temperatures. However, at the same time, the combined use of the two has relatively high requirements for the preparation process and input cost.

However, the application of film-forming additives requires strict control of the addition amount. Excessive addition of VC will cause the SEI film to be too thick, increasing the interface impedance, while excessive VEC will result in insufficient film formation, affecting the initial cycle efficiency. The combination of the two has higher requirements for the preparation process, which leads to an increase in cost.

#### 3.3.2. Flame-retardant additive

Flame retardant additives can reduce the flammability of lithium-ion battery electrolytes, thereby lowering the risk of battery combustion and explosion. At present, phosphorus-nitrogen compounds

and halogenated phosphate esters are the mainstream composite flame retardant additives. Most flame retardant additives are phosphine organic compounds and their halogenated derivatives that reduce combustion reactions by capturing free radicals, lower the self-heat release rate, and delay the initial self-heat release temperature [9]. Among halogenated phosphates, both F and P have flame-retardant effects. The synergistic effect of the two is more obvious, and F atoms help form a more excellent and stable SEI film to improve the stability of lithium-ion batteries. Studies have shown that chlorinated phosphate esters synthesized from methanol and hexachlorocyclotriphosphate can reduce the self-heating rate of batteries by 70% without affecting battery performance. Adding 5% flame retardants to the phosphorus-nitrile additive can make the electrolyte of lithium-ion batteries difficult to ignite or non-flammable without affecting its performance [10].

In applications, the amount of flame retardant additives added needs to balance the safety and electrochemical performance of the battery. Some halogenated phosphate esters have certain toxicity, and the high viscosity of phosphorus-nitrogen compounds hinders the flow of the electrolyte, so they need to be used in combination with low-viscosity solvents.

#### 4. Conclusion

This research topic has conducted a comprehensive analysis of the solvent, electrolyte (solute), and additives in the electrolyte. By analyzing whether electrolytes composed of different components can effectively enhance the performance of lithium-ion batteries, several important variables affecting battery performance have been summarized.

Ether-based solvent electrolytes have superior low-temperature performance, and the interfacial film they form can enhance the stability and safety of batteries, but their high-temperature performance is insufficient. Sulfone solvents have high thermal stability, but their viscosity at low temperatures is high and their low-temperature performance is slightly poor.

In addition, LiDFOB can effectively inhibit the corrosion of LiFSI on aluminum current collectors, enhancing stability and safety. On the other hand, LiFSI can effectively make up for the insufficient thermal stability of  $\text{LiPF}_6$ , and in combination, it can enhance the stability of the electrolyte under different conditions. The combination of the three can form a more stable and dense SEI film, thereby extending the battery life. However, the mixed use of the three lithium salts requires a complex preparation process and high costs. If they are not properly combined, it may affect the performance of the battery.

The use of vinylene carbonate (VC) and vinyl carbonate (VEC) compounded as film-forming additives can combine the advantages of both to make up for their respective shortcomings. The fast film-forming speed of VC can improve the low-temperature charging and discharging efficiency of batteries, and the good chemical stability of VEC can increase high-temperature stability. Therefore, the combination of the two can further optimize the performance of the SEI film. Enable the battery to maintain good performance over a wider range of temperatures. However, when the two are used in combination, the proportion needs to be precisely controlled, and the cost is relatively high. At present, among the composite flame retardants, chlorinated phosphate esters can reduce the self-heating rate of batteries, and the addition of flame retardants to phosphorus nitrogen ene additives can make lithium-ion batteries difficult to ignite or non-flammable.

In conclusion, these studies have significant practical significance for improving the performance of lithium-ion batteries under different conditions. For different application environments, cost budgets, and process conditions, different solvents are selected or compounded, electrolytes are mixed, and additives are compounded to enhance battery performance and make the battery safer

and more stable. Although there are still limitations in these aspects at present, these factors still provide valuable references. Through the future development and research of more types of solvents, electrolytes and additives, the performance and application scope of lithium-ion batteries can be greatly improved, and they can develop in a safer and more stable direction.

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