The Effect of Temperature on the Electrolyte of Lithium Battery and the Strategy for Additive Use

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Abstract. Lithium-ion batteries have found extensive applications in portable electronic devices, energy storage systems, and various other fields. However, temperature has an important impact on the performance of LIBs in all aspects. In low-temperature environments, common commercial LIBs cannot avoid the problems of sharp drops in energy and power density, increased internal resistance, and the consequences of lithium dendrites, severely limiting their applications in key fields such as aerospace and polar exploration. On the other hand, high-temperature environments lead to rapid ion migration and electrochemical reactions, causing more pronounced exothermic side reactions, ultimately resulting in thermal runaway of the battery. The simplest and fastest way to solve these problems is to add additives to the electrolyte. Therefore, this article first introduces the effects of different temperatures on LIBSs electrolytes and their properties. Then, the application of different additives in LIBs was emphasized, aiming to provide valuable insights for future research on lithium-ion battery performance.

Keywords: Lithium battery, additive, electrolyte.

1. Introduction

The continuous extraction and use of conventional fossil energy sources have led to severe environmental pollution and an increasing greenhouse effect. The current energy structure is gradually shifting from traditional fossil energy sources to low-carbon, clean, and sustainable secure energy sources. Electrochemical energy storage technology is currently the most promising clean energy storage technology. Among various electrochemical energy storage devices, lithium-ion batteries (LIBs) are widely used in aerospace, automotive, energy and other fields due to their outstanding advantages such as high energy density, good safety performance, and long service life.

As technological advancements continue, higher demands are placed on electrochemical energy storage devices, including requirements for higher energy density, enhanced safety, and improved stability. Positive electrode, negative electrode, diaphragm, and electrolyte are the four essential parts of a LIB. Li/Li^+ ions are stored in the positive and negative electrode materials, while the electrolyte primarily facilitates the transit of Li^+ ions, the separator guards against short circuits, and the channel for Li^+ ion transfer. The operational concept of lithium-ion batteries is depicted in Figure 1 [1].

However, the current state of lithium-ion battery systems is not yet perfect and leaves room for improvement, especially in terms of temperature limitations and safety issues. Incidents of thermal runaway in lithium-ion batteries due to misuse are frequently reported. In pursuit of enhanced battery safety, researchers have made continuous efforts, including optimizing the composition of the electrolyte, enhancing separator performance, and establishing battery management systems. Electrolytes, as a critical component of LIBs, have a direct effect on their performance. Therefore, enhancing the functional role of the electrolyte in lithium batteries is a crucial pathway to improving various battery performance metrics. Among the components of the electrolyte, additives stand out due to their small quantities and significant effects. They can markedly improve various aspects of lithium battery performance without significantly increasing production costs or altering manufacturing processes. Consequently, this paper analyzes the influence of temperature on lithium-ion battery electrolytes and proposes distinct additive usage strategies for high and low-temperature conditions.

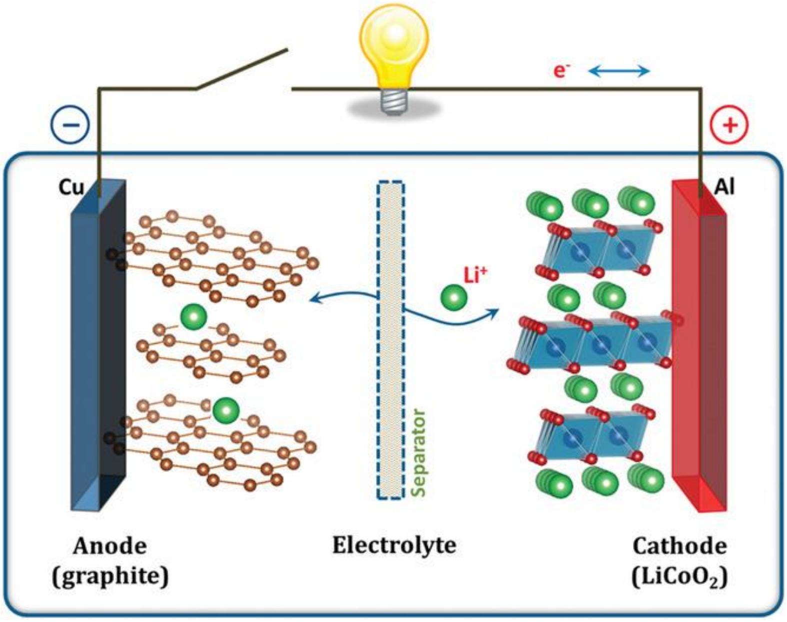

Figure 1. Problems in low-temperature LIBs [1].

2. The effect of temperature on LIBs electrolytes

Electrolyte serves as the carrier for ion conduction in batteries, comprising lithium salts, solvents, and additives. Viscosity in the electrolyte is a crucial parameter that determines the efficiency of lithium-ion ion transport and its film-forming ability. Since lithium ions are highly unstable in aqueous systems, non-aqueous and non-protonic organic solvents are typically chosen. Ideally, solvents should possess low viscosity and high dielectric constants. However, high dielectric constant solvents often exhibit higher viscosity. Therefore, in practical applications, a combination of several solvents is often used to achieve a more ideal solvent. Currently, commonly used organic solvents for lithium-ion battery electrolytes include carbonates, ethers, and carboxylates. The unique performance of Li ions endows LIBs with many advantageous characteristics, such as high energy density and fast charging, such as high energy density and fast charging. Commonly used lithium salts include $LiPF_6$, $LiClO_4$, $LiBF_4$, LiBOB, LiTFSI, and $LiAsF_6$, with $LiPF_6$ being the most frequently used lithium salt [2]. Additives refer to small amounts of non-energy storage substances added to the electrolyte, and their judicious incorporation can effectively enhance and improve battery performance. Electrolyte additives typically exhibit good stability, are less prone to decomposition at high temperatures, and have excellent compatibility with solvents. Most electrolytes perform well only at room temperature. However, the performance of electrolytes containing additives will not deteriorate at higher temperatures [3].

Figure 2 shows the problems in low-temperature LIBs [4]. The dynamic performance of the graphite negative electrode degrades and the SEI film impedance rises at low temperatures as a result of the increased electrolyte viscosity. This can result in an increase in electrochemical polarization of the battery and significantly lower discharge capacity. An electric car, for instance, that can drive 105 miles at 23.9 °C, can only go roughly 60 miles in -6.7 °C. Low-temperature charging, which can result in the development of lithium dendrites and seriously jeopardize safety, is also extremely risky. The viscosity of the electrolyte diminishes at low temperatures. The active substance's activity reduces as the conductivity does. It will accelerate polarization, produce an early termination of charge, and raise the electrolyte concentration difference. The diffusion rate of lithium ions in the carbon negative electrode will also be slower, which is more significant. Precipitation is a problem with lithium. As the temperature decreases, the reaction rate of the electrode also decreases.

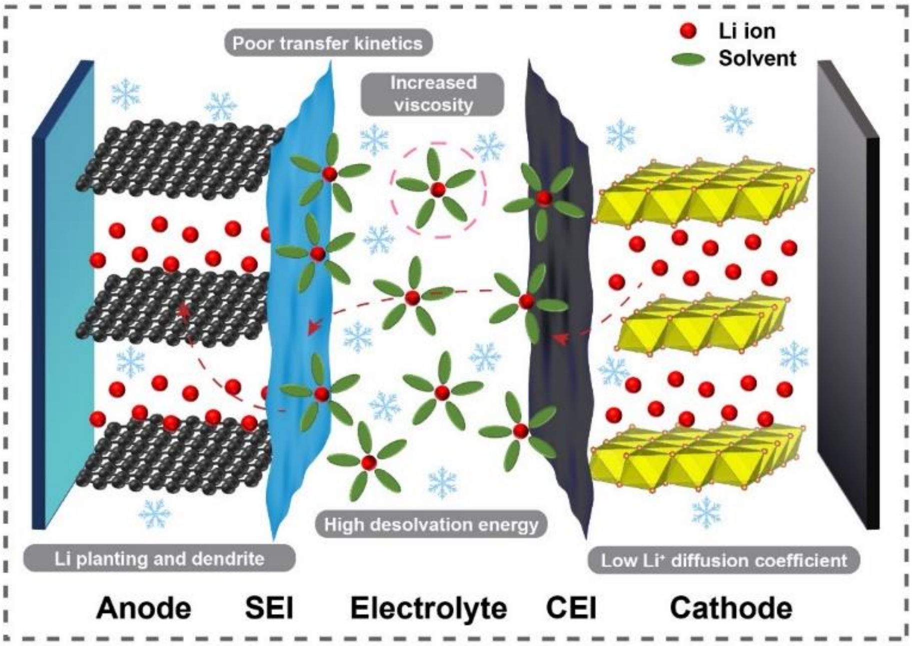

Figure 2. Problems in low-temperature LIBs [4].

The electrolyte's components constantly breakdown in high-temperature conditions, enhancing interactions between the electrodes and electrolyte. The SEI coating thickens concurrently, which reduces interface stability and reduces the effectiveness of lithium-ion transport. Additionally, this creates serious safety risks. In the widely used commercial standard electrolyte LiPF6-ethylene carbonate (EC)/diethyl carbonate (DEC) system, for instance, high temperatures cause the carbonate solvents in the electrolyte to decompose more quickly and produce a lot of CO2 gas, which can cause battery swelling and even leakage or explosion [1].

Commonly employed strategies to address these challenges include: 1) changing the battery electrolyte to reduce viscosity and facilitate lithium-ion conduction; 2) selecting lithium salts that dissociate lithium ions more readily; and 3) adding additives to the electrolyte. Among these strategies, the addition of electrolyte additives (strategy 3) is the most widely used, economical, and effective method [5].

3. Strategies for using electrolyte additives

3.1. Low temperature surroundings

At low temperatures, film-forming additives are commonly used. The principle of these additives is that they preferentially undergo redox reactions at the carbon-negative electrode [6], altering the composition and structure during the SEI formation process, thus promoting the formation of a denser oxide film [7]. Currently, the main types of film-forming additives include ester additives, sulfur-containing additives, lithium salt additives, inorganic additives, and other additives.

3.1.1. Ester additives

The most common ester additive is vinylene carbonate (VC). It works by preferentially grabbing electrons from the electrolyte, reducing them, and then forming an SEI layer across the surface of the carbon-negative electrode to increase battery capacity. Nearly all battery systems respond well to VC while operating at lower voltages. According to research, VC has an effect on the anode as well. Low concentrations of VC in graphite-based batteries preferentially decline at the negative electrode. A performance-equivalent CEI film also develops at the positive electrode as the VC concentration rises. However, VC impairs the thermal performance and safety features of the cathodes in LIBs. Additionally, following high-temperature storage, it may result in increased internal resistance, rendering it inappropriate for use in situations with high temperatures [8]. Therefore, it is often used in combination with other additives.

3.1.2. Sulfur-containing additives

Sulfur-containing additives mainly refer to sulfolane and sulfone additives. Compared to the cyclic carbonate esters mentioned earlier, cyclic sulfone additives have a central sulfur atom with a higher electronegativity than the central carbon atom in carbonate esters. Therefore, they are more easily reduced to form the SEI film. Experiments have shown that when VC is added alone, excessive CO_2 gas is produced. However, when 1,3-propane sulfone (PS) is added, the gas generation decreases by 60% [2]. Additionally, PS is found to form a lower-resistance SEI film on silicon oxide negative electrodes, demonstrating its ability to participate in the formation of a passivation layer, thus protecting the metal electrode material from corrosion. Due to the gas-inhibiting effect of sulfur-containing additives, they are often used in combination with other additives.

3.1.3. Lithium salt additives

Lithium salt additive $LiPF_6$ is currently the most widely used material. However, $LiPF_6$ is highly hydrolyzable and produces HF, which can cause severe corrosion of metal electrodes. Therefore, researchers are focusing on developing more stable novel lithium salt additives, such as lithium bis(oxalato)borate (LiBOB). During the initial charge, LiBOB oxidizes on the cathode surface, forming a stable SEI layer that reduces interface polarization and prevents battery voltage decay [6]. Furthermore, the efficiency of lithium-ion transport within the SEI film formed by LiBOB is higher than from the solid phase of the SEI. However, LiBOB has low solubility, and there is currently a lack of electrolytes with low viscosity that can dissolve LiBOB in large quantities.

3.1.4. Inorganic additives

Inorganic additives modify the SEI film, making it smoother and more even. They can be categorized based on the film formation mechanism into several types: those that enhance the stability of the negative electrode (e.g., CO_2, SO_2), those that inhibit lithium dendrite growth (e.g., $AgPF_6$, $LiNO_3$), additives that enhance cycling performance and safety, and additives that reduce the viscosity of the electrolyte. Inorganic additives themselves are non-flammable and relatively safer compared to organic additives. However, they also face the challenge of poor solubility [6].

In addition, other film-forming additives include silane-based additives, GBL and its derivatives, ionic liquids, anhydride-based additives, and nitrogen-containing additives, among others.

3.2. High temperature surroundings

Currently, common carbonate-based batteries tend to generate volatile gases and undergo electrolyte oxidation in high-temperature environments. This oxidation results in the breakdown of the SEI film, leading to its loose structure and increased thickness. Consequently, the protective ability of the SEI film on the negative electrode material is reduced, and even damaged due to decomposition, allowing the electrolyte to come into direct contact with the electrode material. This ultimately leads to thermal runaway. To enhance the thermal stability of batteries in high-temperature conditions, flame retardant additives can be added to the electrolyte, transforming the flammable electrolyte into non-flammable or less flammable forms. This helps prevent the battery from igniting or exploding under overheating conditions. Since the combustion of the electrolyte is a chain reaction, apart from using inorganic additives as mentioned earlier, the common current solution is to add additives that decompose to produce radicals, which terminate the chain reaction.

Phosphorus-based flame retardant additives are widely used in this field, such as triphenyl phosphate (TPP), triethyl phosphate (TEP), trimethyl phosphate (TMP), and diphenyl phenylphosphinate (CDP), among others. TMP and TEP were among the first flame retardants studied. They decompose at high temperatures to generate PO_2 and HPO_2 radicals, which combine with $H\cdot$radicals produced by organic solvents, thereby terminating the chain combustion reaction. They work by releasing phosphorus-containing radicals (such as $PO_2\cdot$and $HPO_2\cdot$) to prevent the progression of the combustion reaction [9]. For instance, TMP is heated to vaporize into the gaseous state and then decomposes, releasing $PO_2\cdot$ and $HPO_2\cdot$ radicals that combine with H· radicals produced by the organic solvent, effectively terminating the heat-releasing chain combustion reaction. Jia et al. used TEP to obtain a high-concentration electrolyte with 1.2 mol/L of flame retardant and applied it to carbon-silicon negative electrode materials [10]. They discovered the Li^+-TEP structure, which enhanced the stability of the anode cycle. Additionally, they found that the addition of fluoroethylene carbonate (FEC) significantly suppressed the decomposition of lithium salts, forming a robust SEI film rich in LiF. This SEI film could accommodate the volume changes of silicon and maintain the structural integrity of the silicon-carbon electrode, resulting in excellent high-temperature performance for the battery.

4. Summary

In conclusion, this paper has summarized the effects of low and high temperatures on electrolytes and discussed several types of electrolyte additives currently available, emphasizing the significant role of electrolyte additives in enhancing lithium-ion transport efficiency and facilitating membrane formation. Currently, there are several areas for potential improvement in electrolyte additives: (1) avoiding the use of a single type of electrolyte additive. Ideally, a combination of multiple additives that do not interfere with each other's functions can be employed, (2) seeking solvents with better compatibility with the additives, improving their solubility, (3) continuing the development of novel additives to further enhance battery performance.

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