Research Status of Low-Temperature Electrolyte Additives for Lithium-ion Batteries

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Abstract. Lithium-ion batteries have been the most promising energy storage technology in the field of new energy due to their advantages such as high specific energy. With the further expansion of the application range, higher requirements are placed on the low-temperature performance of the battery. The development of suitable electrolyte additives to improve the interface structure of the electrode and the electrolyte is an effective and economically feasible method to improve the low-temperature performance of the battery. This article reviews the research progress of low-temperature electrolyte additives for lithium-ion batteries in recent years. It summarizes the action mechanism of low-temperature electrolyte additives from three aspects: organic solvent additives, lithium salt additives, and new additives. The development of low-temperature electrolyte additives in the next step was prospected.

1. Introduction

The rapid development of the traditional automobile industry has led to serious environmental pollution and a shortage of fossil energy, which has further promoted the development of the electric automobile industry. Due to higher energy density, superior cycling performance and less pollution[1], lithium-ion batteries (LIBs) have gradually replaced lead-acid batteries as the main energy storage device for electric vehicles. However, the discharge capacity and cycle life of lithium-ion power batteries are rapidly reduced under low temperature conditions, which affect the popularization and application of electric vehicles for alpine regions and cold winters. Under low temperature conditions, the poor low temperature performance of LIBs was attributed to low electrolyte conductivity, slow kinetics of charge transfer, increase of the SEI (solid electrolyte interphase) resistance, slow lithium diffusion or to a combination of these factors[2-4]. As the “blood” of LIBs, electrolytes have an important influence on many processes such as liquid phase diffusion, SEI film formation and desolvation reactions. Therefore, the development of low-temperature electrolyte can effectively improve the low-temperature performance of the battery. Electrolyte additives are one of the most economical and effective ways to improve the performance of LIBs. Different types of low-temperature electrolyte additives were studied in this paper.
2. Organic solvent additives

Traditional organic solvent additives are the first additives to be applied to low-temperature electrolytes, usually through the introduction of F, S and other elements to improve the composition of the SEI film.

2.1. F-containing additives

Due to the strong electronegativity and weak polarity of Fluorine atom, the addition of F-containing additives can reduce the freezing point of the electrolyte, increase the flash point, and improve the oxidation stability. Moreover, F can easily react with Li⁺ to form LiF, which can effectively increase the LiF content in SEI membrane and significantly reduce the impedance of SEI film\(^{[5]}\). Fluoroethylene carbonate (FEC) is a single F-substituted product of EC. Its melting point is 17℃, which is lower than that of EC (37℃), and it is one of the most commonly used additives for low-temperature electrolyte. In addition to its excellent film-forming performance, FEC can also effectively improve the low-temperature ionic conductivity of electrolyte\(^{[6]}\). Furthermore, more new F-containing organic compounds have been found to be used as low-temperature electrolyte additives. It has been reported that adding only 2% of N-N dimethyl trifluoroacetamide (DTA) containing three F- can increase the discharge capacity of graphite/Li half cell from 72.2 mAh/g to 114.6 mAh/g at -20℃\(^{[7]}\). In addition, lone pair electrons on the surface of N atoms in DTA will combine with PF₅, The CO₂ generated by the reaction between PF₅ and Li₂CO₃ is reduced, and the gas production in the circulation process is effectively decreased.

2.2. S-containing additives

According to Density Functional Theory (DFT), sulfur has a lower LUMO energy level, so sulfur-containing additives will be preferentially reduced on the surface of the negative electrode. Decomposition products such as Li₂SO₃, Li₂S and ROSO₂Li show better stability, which improve the composition and conductivity of the SEI film. However, Sulfur has many valence states and many structures, which lead to different decomposition pathways and products in different S-containing additives. Jankowski et al.\(^{[8]}\) studied the decomposition products of different S-containing additives, The reduction products of 1,3,2-dioxathiolane-2,2-dioxide (DTD) and sulfopropionic acid anhydride (SPA) contain large amounts of dimeric sulfur-based species, which macroscopically are seen to contribute to create an advantageous SEI. Propane-1,3-sultone (PS) and prop-1-ene-1,3-sultone (PES) additives will undergo a second reduction, resulting in Li₂SO₃ and other inorganic components that are not conducive to ion conduction. By adding 0.5% DTD, the discharge capacity retention rate of the battery at 0.5C can be increased from 66.44% to 68.64% at -20℃. Compared with DTD, the organic products of dimethyl sulfite (DMS) single-electron reduction decomposition is CH₃OSO. The binding energy of CH₃OSO-Li⁺ (−17.34 kJ/mol) is lower, and it is more conducive to improving the low temperature performance of the lithium-ion batteries\(^{[9]}\). Lin et al.\(^{[10]}\)found that the addition of 1wt% phenyl methanesulfonate (PhMS) increased the 100 cycles capacity retention rate of LiNi₀.₅Co₀.₂Mn₀.₃O₂/graphite battery at -10℃ from 54.7% to 73.8%. According to Figure 1, the X-ray photoelectron spectroscopy (XPS) results show that the decomposition products of PhMS, ROSO₂Li and LiS₂, reduce the resistance of the SEI film at low temperatures, which further proves the beneficial effects of ROSO₂Li and other organic reduction products on the low-temperature performance of LIBs.

\(^{[5]}\) LiF content in SEI membrane and significantly reduce the impedance of SEI film

\(^{[6]}\) FEC can also effectively improve the low-temperature ionic conductivity of electrolyte

\(^{[7]}\) Adding only 2% of N-N dimethyl trifluoroacetamide (DTA) containing three F-

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3. Salt additives

LiPF₆ still occupies the leading position of commercial lithium-ion battery lithium salt at present, due to its high solubility and oxidation stability, and moderate price. But the disadvantages of LiPF₆ are poor chemical and thermal stability and insufficient low-temperature performance. The development of new lithium salt is mainly to change the types of anions. Among them, lithium borate and LiPO₂F₂ can effectively improve the film-forming performance, which is beneficial to improve the low-temperature performance of the battery. However, inherent shortcomings prevent them from completely replacing LiPF₆, and can only be used as lithium salt additives.

3.1. Borate lithium salt additives

Lithium Bis(oxalato) Borate (LiBOB) and Lithium Difluoro (Oxalate) Borate (LiDFOB) are the main lithium borates used as lithium additives, mainly due to their good film-forming properties. In the reduction process, LiBOB and LiDFOB release oxalate and F⁻, which promote the formation of the inorganic layer in the SEI film[11]. Compared with LiBOB, the existence of F⁻ in LiDFOB improves the solubility of LiDFOB in organic solvents and reduces the viscosity of electrolytes. At the same time, the impedance of LiDFOB is smaller, which is mainly due to two reasons. One is that LiDFOB can react with LiPF₆ to form a stable compound, LiPF₆C₂O₄, which makes the SEI film uniform and dense, and makes the impedance smaller[12]. Another reason is that after one oxalate in LiBOB is reduced, the other oxalate ring opens and electrochemical polymerization with other BOB⁻, leading to cross-linking reaction, which increases the impedance; However, there is only one oxalate in LiDFOB, and no similar cross-linking reaction will occur[13]. Krause et al[14] also found that the discharge capacity of NCM/graphite battery increased by more than three times by adding 0.10M LiDFOB lithium salt at the temperature of -20°C. However, lithium borate still has the disadvantage that it is difficult to dissolve in chain carbonate, leading to the increase of electrolyte viscosity[15], which is also an important reason that can’t replace LiPF₆ and can only be used as an additive.

3.2. LiPO₂F₂

LiPO₂F₂ is the hydrolysate of LiPF₆ and a component of the SEI. The improvement of low temperature performance of battery by LiPO₂F₂ is mainly reflected in three aspects. The first is that the decomposition of LiPO₂F₂ leads to the increase of LiF content in the SEI, which reduces the impedance of SEI film, showing the effect similar to that of F-containing additives such as FEC[16]. Secondly, the presence of LiPO₂F₂ increases the content of Li₃CO₃, Li₃PO₄F₂ and other inorganic components in the SEI film. Due to the poor solubility of inorganic components in the solvent, it effectively passivates the electrode, prevents the further decomposition of the electrolyte, and inhibits
the growth of lithium dendrite during the low-temperature cycle [17]. The third is that LiPO₂F₂ can be preferentially oxidized at the cathode interface. The formation of the interfacial film can inhibit the dissolution of Mn²⁺ and improve the structural stability of cathode materials during low temperature cycling. Therefore, LiPO₂F₂ is a kind of low temperature additive which is more suitable for the whole battery, and it can improve the interface between positive and negative electrodes.

4. New additives

In addition to traditional organic solvent additives, researchers have also reported various new additives in recent years. Ionic liquids (ILs) extensively used as a new additive of low temperature electrolyte for LIBs because of their attractive properties, including negligible vapor pressure, wide electrochemical potential window and wide liquid ranges. The midazolium cations in ionic liquid additives have good cathode and anode compatibility and high conductivity. The PMMA-IL-TFSI ionic liquid designed and synthesized by Wu et al. [18] can reduce the freezing point of the electrolyte and increase the number of freely moving lithium ions in the system, which greatly improves the conductivity of the electrolyte at low temperatures. Wang et al. [19] synthesized 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) ionic liquid. As a low-temperature electrolyte additive, EMI-BF₄ can combine the high conductivity of EMI⁺ and the excellent film-forming performance of BF₄⁻. The addition of EMI-BF₄ increases the discharge capacity of NCM532/graphite battery from 303.7mAh to 878.7mAh at -30°C.

Siloxane additives used in LIBs have good ionic conductivity and chemical stability, can be used in a wide temperature range [20], and have the potential to be used as low-temperature electrolyte additives. Kim et al. [21] found that polydimethylsiloxane (PDMS)-based additives can participate in the film-forming reaction, and the formed SEI film has stable properties and low impedance. After 50 cycles at -20°C, the capacity retention rate was 89%, which was much higher than that of batteries without PDMS-A (65%). Hydrophilic fumed silica usually has -OH groups distributed on the surface, which are connected to each other through hydrogen bond interactions in a liquid medium to form gels. The porous networks of the gel allow lithium ions to pass through the electrolyte medium, resulting in an increase in the ionic conductivity of the LIB electrolytes. The surface -OH groups can interact with electrolyte components to cause decomposition and affect the formation of the SEI. Hamenu et al. [22] found that by using lithium salt nano-salt (Li-SiO₂) additives, it has an increased ionic power below -20°C. The combined application of the two additives PDMS-A and Li-SiO₂ can improve the low-temperature rate and cycle performance of the battery better than the separate application. It is found through impedance test that the synergistic application of the two additives at -20°C reduces the interfacial impedance from 24.2Ω to 2.4Ω [23], which proved to effectively improve the interface performance of the electrode/electrolyte.

5. Conclusion

The study of electrolyte is the key to improving the low-temperature performance of lithium-ion batteries. Compared with electrode materials, the composition and properties of electrolyte are easier to manipulate and modify in practical applications, and a small amount of additives can play a more obvious effect. Therefore, research in this area is a breakthrough to improve the low-temperature performance of lithium-ion batteries. There are many types of low-temperature electrolyte additives, but their main function is to improve electrolyte ionic conductivity and improve SEI membrane performance. However, there are different in the mechanism of action of different types of additives to improve the conductivity of the SEI film. This article mainly summarizes the different types of low-temperature electrolyte additives, analyzes their mechanism and modification effects, in order to further improve the low-temperature performance of the battery from the additive direction.

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