Research on the Current Status and Improvement Methods of Electrolytes for Lithium ion Batteries

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Abstract. Owing to their high energy density among other beneficial features, lithium-ion batteries (LIBs) enjoy extensive application across sectors including aerospace engineering, civil transportation, and electronic device manufacturing. Nonetheless, the LIBs electrolyte presents certain drawbacks, which contribute to the diminishing performance of these batteries and pose risks to environmental safety. Considering these issues, the paper begins by presenting the operational principles of LIBs and examining the constituents of the electrolyte and discusses the roles of the individual components. Then, the causes of the problems and proposes improvement strategies are summarized. The working stability of LIBs at extreme temperatures can be improved by a series of measures, such as adding flame retardants and optimizing the composition of electrolytes. The aim of the research is to resolve the current problems with LIBs electrolytes and enhance the applicability and stability of LIBs in various practical situations.

Keywords: lithium-ion batteries, electrolytes, improvement methods.

1. Introduction

LIBs are ideal for aerospace, mobile devices, power tools, and electric vehicles due to their high energy density, long life, and wide operating temperature range. [1]. As a result of progress in technology and decreasing expenses, LIBs are becoming more prevalent in vehicle manufacturing, propelling the growth of innovative electric automobiles. These batteries are fundamentally composed of an anode, a cathode, and an electrolytic medium, with the transfer of lithium ions across the anode and cathode facilitating the storage and discharge of power. However, LIBs still face several challenges in the use of organic solvents and corrosive electrolyte salts, which can lead to the generation of flammable gases, increased internal pressure and battery swelling and leakage, posing a risk of explosion. Also, the concern is the short longevity of the electrolyte attributed to the electrolyte degradation, reducing the performance of the battery. To address these challenges, academia and industry are working to improve the technology and performance of LIBs. To mitigate the impact of electrolyte degradation in LIBs, various measures have been taken, including optimizing electrolyte compositions and battery manufacturing processes, and adding flame retardants.

2. Function of Electrolytes

The current LIBs electrolytes are mainly composed of solvent, solute and additives. Situated between the anode and cathode, the electrolyte enables the transfer of lithium ions, thus ensuring the dependable functionality of the LIBs.

2.1. Solvent

The solvent in the electrolyte, as a major component, is responsible for lithium-ion transport. Common solvents include substances such as propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC). These solvents (e.g. EC+DMC, EC+DMC+EMC, etc.) are selected and proportioned to optimize the physical properties, such as viscosity and electrical conductivity. Various solvents have different representative characteristics, e.g., cyclic carbonates including EC and PC have high dielectric constants, which are favorable for the dissolution of lithium solute. In addition, chain carbonates including DMC, DEC, and EMC have low viscosities, which are favorable for the migration of lithium-ions.

2.2. Solute

The primary function of solute is to provide lithium ions, where the commonly used solutes include lithium tetrafluoroborate ($LiBF_4$), lithium hexafluorophosphate ($LiPF_6$) and the new lithium bis(fluorosulfonyl)imide (LiFSI). The choice of solute has a direct influence on the electrochemical performance and the safety of the battery. Illustratively, lithium tetrafluoroborate ($LiBF_4$) boasts a significant melting point and is thermally robust, enabling it to preserve its chemical integrity even at elevated temperatures [2]. Moreover, lithium hexafluorophosphate ($LiPF_6$) exhibits superior ionic conductivity along with reliable chemical stability. These properties make $LiBF_4$ and $LiPF_6$ have a wide range of applications in electrochemical energy storage which is widely used as electrolyte and additive in LIBs.

2.3. Additive

Electrolytes also contain a variety of additives which can be categorized according to their function. The main additives include film former, high/low-temperature stabilizers, overcharge protection agents, flame retardants, multipliers, etc. Usually, additives include vinylene carbonate (VC) and fluorinated ethylene carbonate (FEC), etc. The specific performance of the electrolyte will be enhanced by these additives, such as the electrochemical performance, uniformity of lithium deposition and formation stability of a solid electrolyte interface (SEI) film. Compounds like ethylene carbonate (EC) and dimethyl carbonate (DMC) serve as agents that generate films and decompose during the initial charge-discharge sequence, giving rise to the formation of a solid electrolyte interface (SEI) layer composed of organic lithium salt. SEI layer functions as a protective barrier for the electrodes, preventing them from coming into direct contact with the electrolyte. It is essential in inhibiting unwanted chemical reactions, thereby improving the durability and stability of the battery, as well as maintaining the uniformity of the electrolyte.

The ratio of electrolyte is also a significantly crucial factor affecting the function of LIBs. Too high or too low a ratio will affect the battery life. Take, for instance, an excess level of active materials within the electrolyte can hasten the degradation of the electrode and result in its malfunction; conversely, insufficient amounts of these active materials can diminish the power yield of the LIBs, thereby compromising its longevity.

3. Problems in electrolyte

LIBs electrolytes suffer from multiple problems, including notably capacity degradation, increased internal resistance, reduced rate performance, gas generation, fluid leakage, short circuits, and chemical and physical interactions that can lead to thermal runaway [3]. The specific problems are listed below:

Safety apprehensions: The pronounced flammability of the electrolyte stands as the chief element leading to the risk linked with LIBs. Given its crucial role in battery operation, the electrolyte represents a danger due to its composition of flammable substances. The breakdown of the electrolyte into a vaporizable mixture of gas and liquid may arise due to several stress factors, such as overly high charge levels, extreme temperatures, or internal physical harm in the LIBs, which comprise an organic solvent and a saline solution. Under high pressure, it will form a jet state. When the pressure is low, it will accumulate in a liquid state. Both will burn rapidly under open flames or high temperatures, causing fire or even explosion[4]. Thermal runaway caused by overcharging, short circuit, collision, and extrusion of LIBs is often not detected or resolved in time[5-7], it will lead to fire or explosion. As a mixture of unstable lithium salts and low-boiling-point flammable organic solvents[8-10], the energy released when the electrolyte burns is -3 times the energy it contained. Electrolyte plays a leading role in the entire process of fire and explosion caused by thermal runaway and determines the severity of the accident[11]. At the same time, EC may decompose to produce gas at high temperatures. If there is an excess of EC, the amount of gas generated by decomposition will also increase. It could have an impact on the LIBs's operational security, potentially raising its internal pressure and possibly causing it to swell or experience electrolyte escape.

Lifespan issues: The lifespan of LIBs is closely related to the electrolyte. The type, composition and deterioration over time will all affect the service life of the electrolyte. If the electrolyte concentration (EC) exceeds its ideal threshold, it may lead to a denser electrolytic medium, which can hinder ion transit and increase the LIBs's internal resistance. As a result, these alterations have the potential to reduce the energy generation and compromise the LIBs's efficacy. Furthermore, having too much EC might result in a reduction in the electrolyte's chemical stability, hasten its degradation and utilization, consequently diminishing the operational longevity of the LIBs. The electrolyte's decline also plays a significant role in curtailing the lifespan of LIBs and should not be overlooked. The deterioration of the electrolyte will aggravate the degradation of electrode materials, destroy the solid electrolyte interface (SEI) film that protects electrode materials, and lead to intensified reactions between electrode materials and electrolytes, thereby accelerating capacity loss and shortening cycling life [12].

High-voltage decomposition limitation: LIBs electrolytes will decompose under high voltage, mainly carbonate will undergo a continuous oxidation reaction [13]. The widely employed carbonate-based electrolytic solution breaks down, generating hydrogen and ethylene gases at temperatures exceeding 55°C. Additionally, the solid-electrolyte interphase (SEI) coating the anode's surface begins to lose water and fracture as temperatures surpass 65°C, leading to a swift decline in the storage capacity of LIBs and potentially causing complete battery breakdown.

Extreme temperature impact: The resistance for lithium ions to move will decrease as the viscosity of the electrolyte increases in extremely low-temperature environments, leading to a decrease in their movement speed. In low-temperature environments, the electrolyte may even partially solidify, especially when there is a high melting point solvent in the electrolyte. This solidification phenomenon will not only lead to a reduction in the transmission rate of lithium ions in the electrolyte [14], but also suppression of the reaction on the electrode/electrolyte interface, thereby affecting the charge/discharge performance of the battery. Moreover, the conductivity of the electrolyte will decrease in extremely low-temperature conditions, and the activity of active substances will also decrease. This will increase the concentration difference of the electrolyte and the polarization, which may lead to the premature termination of charging. At the same time, the diffusion speed of lithium-ions in the anode will slow down, and there is a possibility of lithium precipitation. Furthermore, the elevated viscosity and potential solidification will affect the compatibility of the electrolyte with the other components, which will result in a decrease in the performance of the LIBs. Lithium metal easily precipitates on the negative electrode and reacts with the electrolyte when the temperature is low. Building up of material on the solid electrolyte interface (SEI) membrane can result in increased thickness, which in turn may cause an increase in the battery's internal resistance. High temperature environments are still a challenge to the stability of LIBs electrolytes. In addition to the problem of high-temperature decomposition, the problem of thermal runaway still cannot be ignored. For example, for EC-based batteries, their thermal runaway accidents have attracted much attention in the academic community. Thermal runaway will cause the rise temperature, burn or even explode. The main reason for thermal runaway is that the electrolyte of EC-based batteries contains organic components (such as EC) that are flammable and thermally unstable. Under high temperature or extreme conditions, the organic components undergo decomposition reactions and release a large amount of flammable gas. After the gas reaches the ignition point, it burns violently[15].

Lithium diffusion rate limitation: The limiting factors for ion diffusion in the electrolyte of Li-ion batteries mainly include the electrolyte viscosity, the electrolyte salt solubility, the Li^+ desolvation energy barriers, the pore size and shape of the diaphragm. The Li^+ desolvation energy barrier refers to the difficulty of separating Li^+ from the solvent, and the barrier directly affects the Li^+ transport efficiency in the battery and the overall performance of the battery. The battery's discharge capability and charging rate can be impacted by an increase in internal resistance caused by the increased Li^+ desolvation energy barrier. [16].

4. Improvement methods of the electrolyte

4.1. Impact of Flame retardants on the Safety of Electrolytes

Commercial LIBs often use a volatile, low flash point, flammable carbonate-based electrolyte. The electrolyte can undergo further redox reactions with cathode and anode materials during the thermal runaway of batteries, releasing flammable gases such as CO, CH3, C H4, H, etc., and even triggering a fire or explosion. Studies have shown that the addition of flame retardants can significantly improve the flame retardancy of electrolytes and delay the thermal decomposition process, thus improving the thermal stability and cycling performance of batteries [17-19]. Therefore, the safety risk of the battery under extreme conditions such as elevated temperature or short circuits can be suppressed.

There are two types of flame retardants that mainly used in LIBs: phosphate flame retardants and aluminate flame retardants. Phosphate flame retardants, such as ammonium phosphate, sodium tripolyphosphate, ammonium polyphosphate, etc., can form phosphoric acid and the lithium phosphate protective film inside the lithium battery through thermal decomposition, which not only isolates the oxygen but also reduces the amount of oxygen. It also reduces heat transfer. This type of flame retardant has the characteristics of low toxicity, high stability and non-volatility, which is suitable for various types of LIBs. Aluminate flame retardant, the main component of which is aluminum hydroxide, can expand and release a large amount of water vapor by absorbing heat when there is a failure inside the LIBs, then forming a gas phase barrier and providing a flame retardants effect. This kind of flame retardant can play a good flame-retardant effect at high temperatures, which is also applicable to various types of lithium batteries.

4.2. Optimization of Electrolyte Composition

Enhancing both the makeup and the proportions of the electrolyte constituents can considerably heighten the efficacy and dependability of LIBs, thus accommodating the requirements of various usage contexts. It is crucial to factor in the influence of the Solid-Electrolyte Interphase (SEI) layer as well as the interplay between the electrolyte and electrode boundaries on ionic movement to advance the battery's performance at reduced temperatures [20]. The performance of Li-ion batteries is prone to rapid degradation at low temperatures, the main reasons are a decrease in the charge transfer rate and an increase in competitive reactions. Choosing an appropriate electrolyte is crucial for low-temperature performance. Improving the performance of LIBs in cold environments involves adjusting the composition and physicochemical properties of the electrolyte. By adding low melting point and low viscosity components and reducing the ethylene carbonate (EC) content in the solvent, the viscosity and eutectic point of the electrolyte at low temperatures can be effectively reduced. The amorphous electrolyte obtained by mixing two solvents, EC and poly (ethylene glycol) dimethyl ether greatly improves the performance of the electrolyte at low temperatures, and its conductivity can be improved to 0.014 mS cm^{-11} even at -60°C. By mixing the commercially available electrolyte salt and lithium hexafluorophosphate ($LiPF_6$), a high-impedance SEI film can be formed, resulting in poor low-temperature performance. It is therefore essential to develop new lithium salt. Integrating additives designed for cold environments enhances the enduring performance of lithium-ion cells when operating in chilly temperatures. Different types of additives play different roles. First, fluorine-containing additives. Testers found that adding fluorine-containing additives to the LIBs electrolyte helps reduce the impedance of the SEI film and increase the content of LiF, thereby improving the low-temperature stability of LIBs [21]. Among many fluorine-containing additives, the most common one is fluoroethylene carbonate [22]. At the same time, sulfur-containing additives can effectively reduce the impedance of the electrode because sulfur has a lower LUMO energy level and will be preferentially oxidized on the surface of the negative electrode material and form substances such as LI S on the electrode surface [23]. In addition, silicon-containing polymers are also often used as additives for low-temperature electrolytes of LIBs because they have good ionic conductivity and chemical stability [24]. Polydimethylsiloxane (PDMS)-derived copolymers exhibit characteristics including low dielectric constants, resistance to oxidation, non-stick qualities, and chemical unreactivity. Research has demonstrated that introducing functional groups to the surface enhances both the electrochemical performance and the interface stability in LIBs when operated under cold conditions, while also significantly reducing the development of lithium dendritic structures [21].

5. Conclusion

At present, the technical performance of electrolytes has reached a relatively mature and perfect level. In solving the safety and stability problems, optimizing solvent composition and introducing flame retardant materials such as phosphate flame retardants and aluminate flame retardants have been proven to be effective ways of improvement. Advancements in electrolyte technology are gaining momentum, and the precise calibration of electrolyte mixtures is poised to greatly enhance the performance and power retention of lithium-ion cells, leading to boundless opportunities in harnessing their full capabilities.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

Reference

[1] Zhang Wenjing, Xiao Wei, Yi Yahui, Qian Liqin. Research Progress on Safety Modification Strategies of Lithium-ion Batteris. Energy Storage Science and Technology[J], 2024, 08

[2] Shang Junli, Zhao Qingyun, Liu Dafan. Preparation and characterization of lithium tetrafluoroborate electrolyte salt for lithium-ion batteries[J]. Inorganic Chemicals Industry, 2015, 47(7):4. DOI: CNKI: SUN: WJYG. 0.2015-07-029.

[3] YK Liu, CZ Zhao, J Du, XQ Zhang, AB Chen, Q Zhang, Small, 2023•Wiley Online Library

[4] Hu We, Experimental study on the effect of TDCPP / PFPN flame retardant on the flammability of electrolyte. Southwest Jiaotong University 2022

[5] Xu K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries[J]. Chemical Reviews, 2005, 104(10): 4303-

[6] Bandhauer T M, Garimella S, Fuller T F. A critical review of thermal issues in lithium-ion batteries[J]. Journal of the Electrochemical Society, 2011,158(3): R

[7] Chen Z H, Qin Y, Ren Y, et al. Multi-scale study of thermal stability of lithiated graphite[J]. Energy and Environmental Sciences, 2011,4(10): 402

[8] Etacheri V, Marom R, Elazari R, et al. Challenges in the development of advanced Li-ion batteries: a review[J]. Energy and Environmental Sciences, 2011,4(9): 3

[9] Spotniz R, Franklin J. Abuse behavior of high-power, lithium-ion cells[J]. Power Sources.2003,1(13): 81-100.

[10] Aurbach D, Talyosef Y, Markovsky B, et a1. Design of electrolyte solutions for Li and Li-ion batteries:areview[J]. Electrochim Acta, 2004, 50: 247-254.

[11] Eshetu G, Grugeon S, Laruelle S, et al. In-depth safety-focused analysis of solvents use dinelectrolytes for large scale lithium ion batteries[J]. Physical Chemistry Chemical Physics, 2013, 15(23): 9145

[12] MengchuangLiua, ZiqiZengb,*, HuiYanc, QiangWub, YuankeWub, WeiLiub, ShengLeib, CongLiaob, XinpingAid, ShijieChengb, JiaXieb, Multilevel regulation of Li^+-solvent interaction for fluorophosphate-based nonflammable electrolyte enabling lithium-ion batteries with long calendarlife, Chemical Engineering Journal 496(2024)154146

[13] Xing Lidan, Xu Mengqing, Li Weishan. Research progress of electrolytes for high-voltage lithium-ion batteries[J]. Scientia Sinica Chimica, 2014(8):9. DOI:10.1360/N032014-00114.

[14] LI Zeheng, XU Lei, YAO Yuxing, YAN Chong, ZHAI Ximin, HAO Xuechun, CHEN Aibing, HUANG Jiaqi, BIE Xiaofei, SUN Huanli, FAN Lizhen, ZHANG Qiang A review of electrolytereducing lithium plating in low-temperature lithium-ion batteries. Energy Storage Science and Technology[J]. 2024(07)

[15] Liu Zhihao, Prof. Deng. Electrical Characteristics and ThermalSafety of Lithium-ion Batteries forAerospace Applications Based on High-Safety Electrol, Chongqing Jiaotong University 2024.

[16] Kikuko Hayamizu, Direct relations between ion diffusion constants and ionic conductivity for lithium electrolyte solutions, Electrochimica Acta 254 (2017) 101–111

[17] LI X,LI W K,CHEN L,et al.Ethoxy (pentafluoro) cyclotriphosp-hazene (PFPN) as a multi-functionalflame retardant electrolyte additive for lithium- ion batteries[J].Journal of Power Sources, 2018,378:707-716.

[18] YANG Y P,JIANG J C,HUANG A C,et al.3- (Trifluoromethyl)benzoylacetonitrile:A multi-functionalsafe electrolyte additive for LiNi0.8Co0.1Mn0.1O2 cathode of high voltage lithium- ion battery[J].Process Safety and Environmental Protection,2022,160:80-90.

[19] Yu Jihang 1, Zhou Peijun 2, Jiang Yangsheng 2. Experimental study on the effect of electrolyte flameretardant additives on needle puncture safety of lithium-ion batteries. Fire Science and Technology.

[20] Wang Yimeng, Xie Leqiong, Sheng Li, et al. Research progress of low-temperature lithium-ion batteries[J]. Chinese Battery Industry, 2022, 26(5): 251-262. DOI:10.19996/j.cnki.ChinBatlnd.2022.05.007.

[21] YAN RAN, Research Progress of Low Temperature Electrolyte Additives for Lithium Ion Batteries, Jiangxi Chemical Industry[J],2024, 40(03).

[22] FENG T,YANG G,ZHANG S,et al. Low-temperature and high voltage lithium-ion battery enabled by localized highconcentration carboxylate electrolytes[J]. Chemical Engineering Journal,2022,433:134138.

[23] GUO R,CHE Y,LAN G,et al. Tailoring lowtemperature performance of a lithium-ion battery via rational designing interphase on an anode[J]. ACS Applid Materials&Interfaces,2019,11(41):38285-38293.

[24] LI Z H,YAO Y X,SUN S et al. 40 years of lowtemperature electrolytes for rechargeable lithium batteries[J].Angewandte Chemie-International Editon,2023,62(37):e202303888.