Research Progress on the Safety of Lithium Ion Battery Materials

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Abstract: Lithium-ion batteries have received much attention as one of the key technologies in energy storage technology. With the development of the new energy field, the energy density carried by lithium-ion batteries is also increasing, and users are paying more and more attention to battery safety. At present, there have been many accidents related to lithium-ion battery fire and explosion around the world, some of which have caused serious threats to human normal life activities and human health. These safety issues are a message to us - ensuring that the use of batteries is safe is critical, especially before considering high energy density battery systems for future applications, must address their safety issues. The purpose of this review is to summarize the root principles of lithium-ion battery safety problems from the three aspects of electrolyte, positive and negative electrode, and focus on the latest progress in the field of material design, aiming to further enhance people's understanding of battery safety and further develop the battery market in the future through this article.

1 INTRODUCTION

In recent years, in response to the scientific concept of green environmental protection, lithium-ion batteries (LIB) have been applied on a large scale in many industries because of their advantages such as high unit energy, fast discharge efficiency and long working life (Tarascon and Armand, 2001; Goodenough and Kim, 2010 & Armand and Tarascon, 2008). Typically, a lithium-ion battery consists of a positive electrode, an anode, and a diaphragm. The positive electrode is usually made of lithium cobaltate (LiCoO2), the anode is made of graphite, and the diaphragm is made of polymer materials such as polypropylene (PP) and polyethylene (PE). The electrolyte consists of LiPF6, ethylene glycol carbonate (EC), consists of at least one phosphate acid salt and one or more flame retardant additives.

The safety of the battery is an important consideration, and although it performs well under normal conditions of use, safety hazards such as overcharging, short circuiting, and high temperatures may occur under conditions of abuse (Balakrishnan et al., 2006; Wang et al., 2012; Wen et al., 2012; Bandhauer et al., 2011 & Doughty and Roth, 2012).

In order to ensure that the battery can run safely and smoothly, it can usually be protected by two ideas: external physical detection and internal micro-regulation. External protection mainly relies on small physical electronic monitoring equipment such as gas sensors and pressure detectors, although these devices are designed and manufactured as small and fine as possible, but most sensors still need to be equipped with specific functional devices (such as heating disks, etc.), and the demand for these components also increases the space occupied by the matched battery and its weight. The out-of-control environment of hot pressing often increases the risk of battery safety accidents. The internal protection scheme is mainly through design or reaction modification to provide an intrinsically safe and structurally reasonable material for the manufacture of battery components, and this scheme is also considered to be the "ultimate" solution to ensure battery safety. The purpose of this review is to summarize the existing safety issues of lithium-ion batteries and to introduce the design of relevant safety materials from three aspects: cathode, anode and electrolyte, in order to improve the safety of lithium-ion batteries and to promote the future development and practical application of lithium-ion battery material safety.

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2 REASONS FOR SAFETY PROBLEMS WITH LITHIUM-ION BATTERIES

The organic liquid electrolyte in the lithium-ion battery is inherently flammable, which also leads to the easy loss of control of the battery under high heat and pressure environment, which is one of the biggest difficulties facing the safety of the lithium-ion battery system. Therefore, fully understanding the causes and processes of lithium-ion batteries in high heat/pressure environment out of control, targeted design of the functional materials of each part of the battery, can better improve the safety and reliability of lithium-ion batteries. For lithium-ion battery thermal runaway inducement, can be roughly divided into three categories: collision runaway, electrical runaway, thermal runaway.

Collision runaway is due to the partial rupture of the diaphragm caused by mechanical deformation of the battery such as collision, extrusion, acupuncture, etc. Electrical runaway is mainly due to the penetration of the diaphragm during the battery charging and discharging process, and thermal runaway is due to the high-temperature environment caused by overheating resulting in a large area collapse of the diaphragm, and the result of the destruction of the diaphragm caused by these three inductions will eventually lead to an internal short circuit inside the battery. A series of safety problems caused by excessive local current. Usually different incentives caused by the battery out of control, the phenomenon will have a certain difference, but the mechanism is similar.

3 ELECTROLYTE

The safety of lithium-ion batteries depends largely on the characteristics of their electrolytes. The electrolyte acts as a channel for the transport of lithium ions within the battery and is usually composed of organic solvents and lithium salts. The safe and efficient operation of batteries often requires electrolytes with high ionic conductivity, wide electrochemical Windows, high safety and low cost. However, the safety problem of electrolyte flammability is a major difficulty faced by safety performance.

At present, many researchers mainly use flame retardant additives to reduce the problem of electrolyte flammability. These additives are mainly based on organophosphorus compounds or organic halogenated compounds. However, most of these additives have structural instability, low toxic halogens in the ingredients may cause environmental pollution and other problems, in order to avoid the above problems, organophosphorus compounds because of its efficient flame retardancy and environmental friendliness and attention, become the first choice of flame retardancy additives. The mechanism of action of these phosphorous compound flame retardants is usually to inhibit the transfer of free radicals during the combustion process. At high temperatures during combustion, phosphorous compounds produce phosphorous free radicals due to decomposition reactions, and such substances can inhibit or even terminate the free radicals responsible for continuous combustion generated during the propagation of the chain reaction (Granzow, 1978). However, phosphorus-containing flame retardants can effectively reduce the flammability of the electrolyte, but also have a certain impact on the working performance of the battery. In view of the adverse effects of such additives, some scientists have proposed to modify the microscopic molecular structure of phosphorous compounds as an idea and successfully put into practice a variety of schemes: fluorination of phosphoric acid compounds containing alkyl with fluoride to obtain additives with significantly improved stability and flame retardant effect (Pires et al., 2015). Choose organic molecules with excellent flame retardant properties and at the same time have a protective shell (films), such as dimethylallylphosphonate, where allyl polymerizes on the graphite surface and forms a stable SEI film, effectively preventing harmful side reactions (Jin et al., 2013). The use of cyclic phosphazene instead of organophosphorus additives (such as fluorinated cyclophosphazene) enhances its electrochemical compatibility (Xia et al., 2015). In addition, researchers have proposed the preparation of a new heat-triggered fiber protective diaphragm, flame retardants can be polymerized as raw materials to form a protective shell, and these shells are further stacked to form a diaphragm through the polymer processing process, so as to achieve the purpose of effective flame retardant (Figure 1).

4 CATHODE MATERIAL

Cathode materials are a key component of lithium-ion batteries and require a number of properties to ensure battery performance and safety. These characteristics include high capacity, stable structure, stable voltage, good cycling performance and easy preparation.

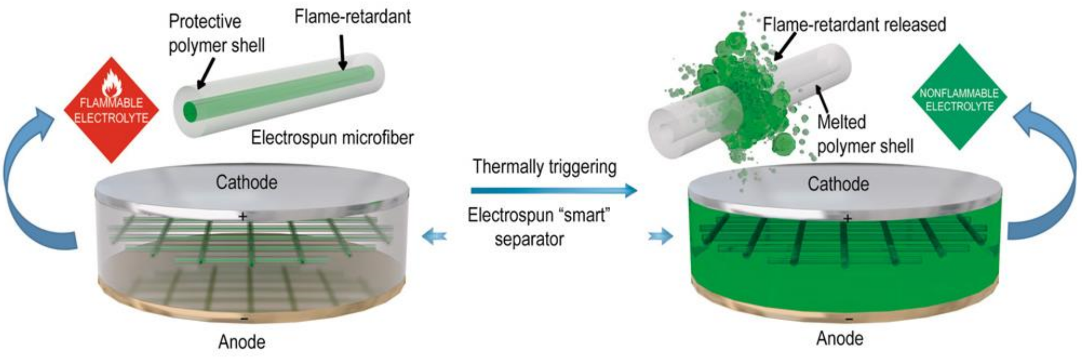

Figure 1: Schematic diagram of the "smart" electrospinning diaphragm of a lithium-ion battery with heat-triggered flame retardant properties (Liu et al., 2017).

The operation of cathode materials directly affects the safety performance of the entire battery. There are very many choices of lithium-ion battery cathode materials in the current market, among which lithium cobalt oxide is the first choice for very many electronic products, while lithium nickel cobalt manganese oxide is the leading emerging material, and lithium nickel cobalt aluminate and lithium iron phosphate are also materials that can't be ignored (Zhang et al., 2024). Among them, lithium nickel cobalt manganese oxide ternary cathode materials (LiNixCoyMn1-x-yO2, abbreviated as NMC) have become the research hotspot of mainstream cathode materials for lithium-ion batteries due to their high specific capacity.

NMC cathode materials may face the following problems during the cycling process: (1) lithium-nickel mixing affects the normal de-embedding of lithium ions, resulting in capacity loss and lower diffusion coefficients of lithium ions, which affects the performance of the batteries; (2) the polycrystalline secondary particles of NMC are susceptible to cracking and fragmentation during the cycling process, especially at high temperatures or high pressures; and (3) the Surface side reactions may lead to cell blistering or explosion.

In response to the above problems, some existing commonly used NMC material modification methods include: (1) preparation of small-particle single crystals to avoid inter-crystalline cracks and fragmentation, and to improve structural stability and cycling performance. For example, by preparing agglomerated and single-crystal LiNi0.8Co0.1Mn0.1O2, the capacity of 0.1C is 216.3mAh/g and 213.7mAh/g at 3.0-4.3V, respectively. The thermal decomposition temperature of agglomerated ternary cathode materials in the charging state of 4.3V is 208℃, while the single-crystal type is 216℃ and the amount of heat release is lower, so the thermal stability is better. By changing the crystal morphology of the material, the monocrystalline structure can enhance the structural stability while ensuring the capacity, improve the cycling performance and increase the thermal decomposition temperature, thus enhancing the safety of the battery (Zhao, 2020). (2) Elemental doping, the introduction of metallic or non-metallic elements to reduce cation mixing, enhance the structural stability and lithium ion diffusion efficiency, such as Wang et al. synthesized two-dimensional porous B, N co-doped carbon/titanium nitride (BNC-TN) composites by hydrogel and ionothermal methods (Wang, 2023), which can be clearly seen that its elemental doping has been improved. Using this method can effectively improve the reduction of diffusion coefficient due to lithium-nickel mixing, and ensure that its surface side reactions are reduced to improve its safety. (3) Surface coating, utilizing stable materials to isolate cathode materials from electrolyte contact and improve cycle stability and thermal safety. By wrapping other highly stable materials, such as phosphate, fluoride, solid oxide, etc., outside the ternary cathode materials, the ternary cathode materials are isolated from direct contact with the electrolyte due to the good thermal and structural stability of the wrapped materials (Tian et al., 2023). From the experiments of Li et al. who used poly-3-octylthiophene as a wrapping material for surface modification of the cathode material, it is evident that this approach has significantly improved its cycling stability and thermal safety (Li, 2023).

In general, in order to solve the safety problems of mixed rows, fragmentation and side reactions in NMC cathode materials, small-particle single crystals are generally used to avoid electrode fragmentation, and elemental doping and surface coating methods are used to reduce the generation of lithium-nickel ion mixed rows and side reactions, so as to improve the electrochemical performance and service life of the overall battery, as well as safety and stability in multiple cycles.

5 ANODE MATERIAL

Early lithium-ion batteries were made directly from lithium metal, but dendrite lithium was often present in the charge and discharge process (Figure 3), causing extremely serious safety hazards. The advent of rocking chair batteries solved this challenge by successfully bypassing dendrite lithium, and I use a layered approach here to solve the lithium-ion storage problem (Wang et al., 2018). At the same time, when the electrolyte comes into contact with the carbon material, it becomes a very tight and connected layer, called the passivation layer or the solid electrolyte interface, which allows the lithium ions to move in a certain space and prevents the movement of electrons in this space. Although the formation of passivation film will lead to irreversible loss of stored energy during the first charge and discharge process, it is caused by the improvement of battery charging efficiency (Nitta et al., 2015). Therefore, layered materials and passivation films become an important part of battery anode safety. At the same time, adverse reactions such as the formation of lithium dendrites are the main safety hazards. In order to improve the safety performance, the negative electrode material needs to have the characteristics of high efficiency, small volume effect, large reversible capacity, high electrolyte sensitivity, low thermal stability and low impurity content.

The crystallization of the anode material will lead to an increase in the sensitivity to the electrolyte, resulting in a significant decline in performance and cycle stability, and a potential safety hazard. Our purpose is obviously to improve the anode material, so we should discuss the changes of lithium dendrites and solid-liquid films.

The change of solid-liquid film (SEI) thickness is closely related to the attenuation of battery capacity and battery safety, and its decomposition is also one of the important factors affecting battery safety. The main reasons leading to the generation of lithium dendrites are low temperature (Wang, 2017 & Hossain et al., 2006), overcharge (Ohsaki et al., 2005; Dietz et al., 2018 & Li et al., 2001) and high rate charge (Marcicki et al., 2014 & Li et al., 2019). The formation of lithium dendrites may also be caused by an energy imbalance (Gallagher et al., 2015). For all anode materials, high performance generally means lower risk. For example, compared with graphite, the soft carbon material formed by synthesis has better

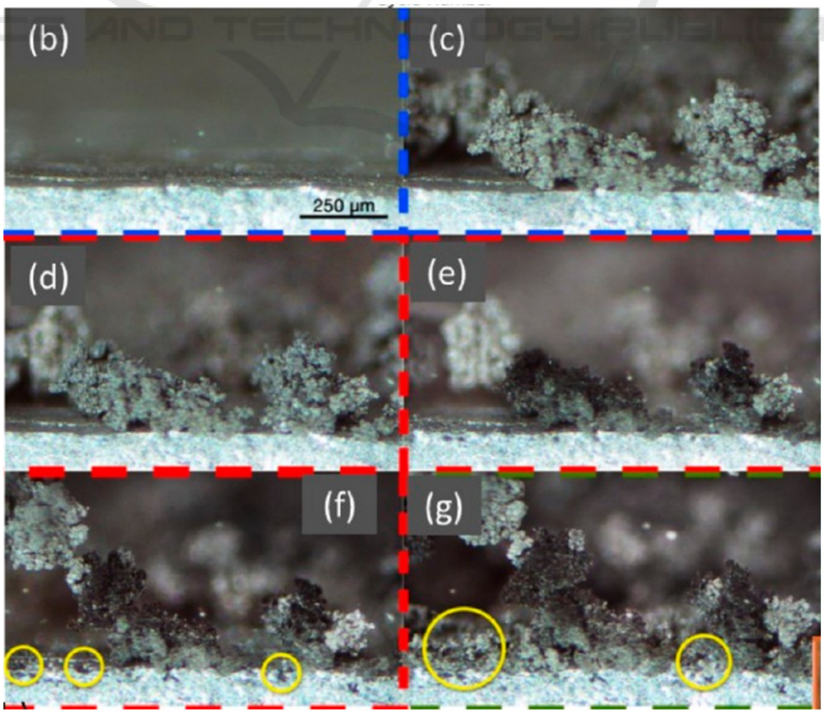

Figure 2: Formation process of lithium ion dendrites (Dhanya et al., 2021).

conductivity at low temperatures and amplification performance under normal use (Broussely et al., 2005). This is mainly due to the low degree of graphitization of soft carbon, which is usually composed of extremely small graphite nanocrystals, thus shortening the diffusion path of lithium (Persson et al., 2010). Under the same overcharge conditions, it was found that less lithium metal was deposited on the carbon surface than on the graphite surface. This may be related to the complete disordered structure of the carbon and the low efficiency of the first cycle of carbon when only a small amount of graphite is deposited. Therefore, mixing hard carbon with graphite has been proposed by some scholars as a way to slow down the formation of lithium ion dendrites. However, this approach is often unsuccessful for several reasons (Liu et al., 2017).

In general, since we want to solve some problems of lithium-ion batteries and increase the safety of lithium-ion batteries, the following methods can be used. First of all, the layered structure of the rocking chair battery can effectively prevent the generation of lithium dendrites, but in practical applications, the layered structure is difficult to achieve. It is also possible to reduce the formation of lithium dendrites by changing the anode material to prevent the formation of lithium dendrites, thereby improving safety.

6 CONCLUSION

Safety is the key criterion to evaluate the commercial application of lithium-ion batteries, which directly affects the future development and application range of lithium-ion batteries. With the increasing demand for battery energy density and rapid charge and discharge, the design requirements for battery materials are also more stringent. To date, researchers have proposed a variety of modified material strategies to solve the dilemma faced by battery safety. This review summarizes the design of related safety materials from the positive electrode, anode and electrolyte. Through research efforts to reduce the flammability of electrolytes, such as the use of environmentally friendly phosphorus-containing flame retardants or structural adjustments to improve electrochemical performance; The cathode material of the battery was improved by preparing small particle single crystal, element doping and surface coating to improve the safety performance and cycle stability of the battery. By studying the layer structure of rocking chair battery to store lithium ions to avoid the safety problems caused by negative dendrite lithium, improve the anode material, control the change of solid-liquid film thickness and decomposition to enhance the overall battery performance.

AUTHORS CONTRIBUTION

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

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