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A Review on Materials for Flame Retarding and Improving the Thermal Stability of Lithium Ion Batteries

Fei Gao[1], *Hao Liu*[1], *Kai Yang*[1], *ChuiTao Zeng*[2], *Shuping WANG*[3,4], *Minghao FAN* [3,4], *Hao Wang*[2,*]

[1] State Key Laboratory of Operation and Control of Renewable Energy & Storage Systems, China Electric Power Research Institute, Beijing 100192, China
[2] College of Materials Science & Engineering, Beijing University of Technology, Beijing 100124, China
[3] Anhui Province Key Laboratory for Electric Fire and Safety Protection of State Grid Anhui Electric Power Research Institute, Hefei 230022, China;
[4] State Grid Laboratory of Fire Protection of Transmission and Distribution Facilities, Hefei 230022, China
[*]E-mail: haowang@bjut.edu.cn

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Lithium-ion batteries (LIBs), featured by high energy density, high power density, excellent cycle performance and environmental friendliness, are widely used in electric equipment, electric vehicles and energy storage. However, accidents related to fires and explosions of LIBs occur frequently worldwide, some have caused serious threats to human life and health. The safety of LIBs is an extremely important and urgent research topic at present. This article aims to review recent key progresses in materials adopted for flame retarding and improving the thermal stability of LIBs from the external and internal parts, and inspire further improvement of various kinds of materials and strategies to improve LIBs safety, especially for emerging LIBs applications in large-scale energy storage fields.

Keywords: Lithium ion battery; Flame-retardant; Thermal stability

1. INTRODUCTION

LIBs, featured by high energy density, high power density, excellent cycle performance and environmental friendliness, are widely used in electric equipment, electric vehicles and energy storage.[1] However, the existing battery system cannot guarantee its safety in essence and exist the possibility of thermal runaway, even burning, explosion and other safety accidents in the use process. In the field of large-scale energy storage applications, the number of batteries used are huge, the energy and power levels of energy storage system are high. Once safety accidents occur, the consequences and hazards are extraordinary serious.

Accidents related to fires and explosions of lithium-ion batteries occur frequently worldwide, some have caused serious threats to human life and health. For example, in January 2013 and January 2014, three fire accidents of Boeing747, happened in Boston America, Takamatsu, Tokyo Japan, respectively; in August 2016, the Samsung Note 7 smart phone suffered explosion; in 16 May 2017, Panasonic announced to recall over 270 thousand LIBs; in 2 July and 29 July 2018, 4MW/12MWh energy storage system caught fire and explosion in Korea and electric scooter caught fire and explosion during charging in China.[2] These incidents are reminders that safety is a prerequisite for batteries. Flame-retardant to avoid the spread of combustion or explosion is necessary to be resolved before the future application of high-energy, high-power and large-scale energy storage battery systems.

From the point view of materials, this article highlights recent key progress in materials for flame retarding and improving thermal stability from external and internal parts and inspires further improvement of various kinds of materials to improve LIBs safety with the assistance of the fundamental's protection strategies.

2. LITHIUM ION BATTERY PROTECTION STRATEGIES

Methods to ensure LIBs safety include external and internal protection strategies. As the fig.1 presents, external protection strategies are to cut off the necessary condition of combustion by using coolant materials, phase change materials and fire extinguishing agents for flame retarding. While internal protection strategies are mainly to improve thermal stability of LIBs from the basic compositions.

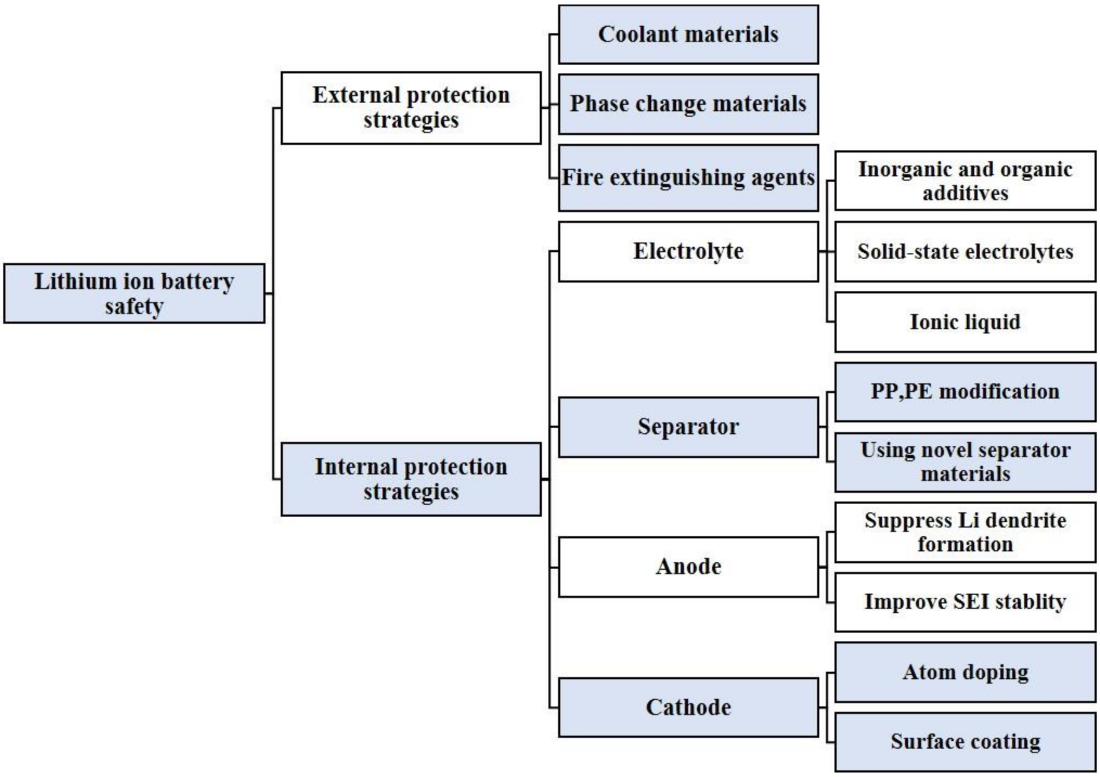

Figure 1. the external and internal protection strategies for safety of LIBs

Single lithium ion battery has an optimal performance at the operating temperature range of 25°C to 40°C, while in large-scale battery application fields the temperature distribution throughout the battery pack in the module should be less than 5°C.[3] Behaviors likes mechanical crush, vibration, overcharge/over-discharged and some other irregularly operate would lead to the temperature increase and distribution inhomogeneous, even thermal runaway to burning or explosion. Reasonable thermal management is of great significance to the performance and safety of batteries.

Battery thermal management system (BTMS) have been put forward an effectively external protection method to improve the safety of high-power LIBs. By adopting advanced technologies from thermal management to thermal safety control, BTMS can suppress battery overheating and its propagation effectively and sufficiently[4], that cannot only guarantee the battery operation performance but also improve thermal safety.

According to the cooling medium, BTMS can be classified as air cooling, heat pipe cooling, phase change material cooling, liquid cooling, and refrigerant direct cooling.[5] The shape of the battery, channel shape and number of channels, diameters of inlet and outlet of channels have important influences on the overall structure and the cooling performance of the battery pack. When necessary, designing the battery arrangement configuration and adding auxiliary device can tune the flow of coolant. These cooling strategies can efficiently reduce the heat resistance between the heat source and the coolant.

Within a normal operating temperature range of LIBs, protection strategies used are to prevent thermal runaway. However, once fire or explode happened, fire extinguishing is the most efficient method to suppress the thermal hazard propagation. As is known, fire or explode occurs only when the material is available to burn, the temperature reaches flash point and the oxygen is adequate, and will not occur if any of these three conditions cut off. Therefore, refrigerant direct cooling, fire extinguishing agent are used to reduce temperature or isolate oxygen for flame-retardant purposes.

Although BTMS with sensing and feedback modules can regulate stacked cells on macroscopic scale, electronic devices such as temperature sensors and pressure valves increase the dead weight/volume of the battery. Such defects are unreliable under thermal/pressure abuse conditions.[6] In addition, the failures of external hardware occur occasionally and become more likely in the abnormal conditions. The potential hazards arising from the inner reactions of batteries are also disconcerting. Internal protection could essentially reduce heat generation and thermal runaway. Hence, developing the reliable internal protection strategy combined with external protection system is particularly necessary for the safety of commercial LIBs. The developed internal protection strategies are mainly focused on improving thermal stability of individual components which include cathode materials, anode materials, separator materials and electrolyte materials, based on material chemistry.[7]

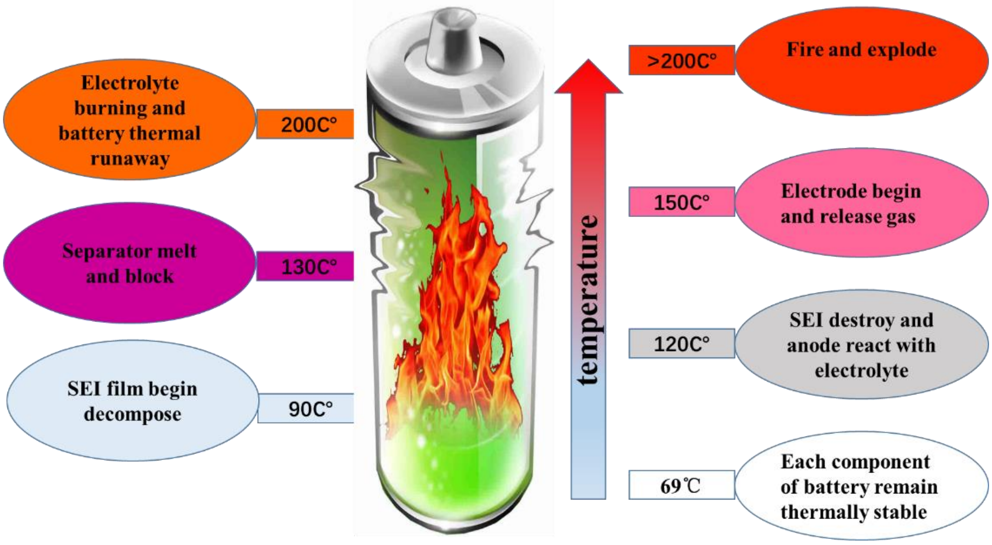

Figure 2. Behaviors of LIBs internal component with the increase of temperature

Fig.2 shows the behaviors of LIBs internal components with the increase of temperature. Each component remains thermal stable below 69°C, while solutions of $LiPF_6$ in organic carbonate solvent mixtures begin to decompose from 69 to 90°C. The solid electrolyte interphase (SEI) film decomposition, anode material reaction with electrolyte and heat generation arise at the temperature of 90 to 120°C. Separator melting and shutting down at 130°C, which caused short circuit and thermal runaway. Cathode material decomposition (150°C, 160°C, 210°C, 265°C and 310°C for $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiNi_xCo_yMn_zO_2$, $LiMn_2O_4$ and $LiFePO_4$, respectively) and cathode material reaction with electrolyte released a lot of gases and heat. When temperature rises up to above 200°C, electrolyte burns and battery explodes. The primary goal of the internal flame-retardant strategy is to cut off the chain reactions. Many attempts have made to modify the component materials inside the LIBs to improve the intrinsic protection capability of battery safety.[8, 9]

The flame-retardant performance of these strategies mentioned above are related to the physicochemical properties of various kinds of materials. As coolant materials have different heat capacity and conductivity. Cathode materials, anode materials, separator and electrolyte materials have different thermal stability, thermal decomposition temperature and flash point, etc. Using different flame-retardant materials may have different flame-retardant effects. To get an insight in the flame-retardant strategies, the following gives a review of materials for flame retarding and improving thermal stability of LIBs.

3. MATERIALS USED IN EXTERNAL PROTECTION STRATEGIES FOR FLAME RETARDING

3.1 Coolant materials

Air and Liquid are some popular BTMS coolant materials used by some famous manufacturing company recent years.

Air as the cheapest and richest coolant material is the most desirable choice for many manufacturers. Air cooling technology with the advantage of simple structure, lightweight, low cost and so on, is one of the most commonly employed and widely used battery cooling approach in electronics and vehicles. In the traditional passive cooling system, heat from the battery transferred to the air coolant and then the heat air exchanged with external air. However, the thermal conductivity and specific heat capacity of air are low so that the cooling capacity is limited. To achieve a high cooling efficiency and maintain the temperature uniformity of battery pack, additional auxiliary design is needed. Compared with the air cooling and cooling system, a better cooling performance can be achieved by using the liquid coolant.

Liquid coolant has a higher thermal conductivity and specific heat capacity than air, so a higher cooling efficiency can be achieved and more heat can be absorbed. Furthermore, the liquid cooling system take less volume and can be placed in a narrower space since the liquid coolant has a bigger density than air.[10] Tesla and General Motors have already applied liquid cooling in electric vehicles and achieved good results. The working fluids for battery liquid cooling coolant mainly include mineral oil[11], refrigerant[12], water[13, 14] and glycol[15], etc.

Though liquid cooling has a good cooling efficiency, these strategies need external power supply to keep the liquid flowing, which increase additional energy consumption. Heat pipes as an efficient heat exchanger, conduct heat through latent heat, do not need external power supply used in the BTMS. Another remarkable advantage is lightweight, compact structure and flexible geometry. [16-18] The heat pipe is a hermetic container consisted of compensator and evaporator. The working fluid evaporated from evaporator to the condenser, and transported back to the evaporator by capillary wick.[19] Researchers have used nanoparticles of different metals (Cu, Ag, and gold, etc.), metal oxides (Al_2O_3, CuO, MgO, ZnO, TiO_2 and SiO_2, etc.) and several other materials suspended in water as the working fluid of heat pipes.[20] Cmbining with other cooling systems, Heat pipes could achieve better cooling performance.[21] However, expensive manufacturing materials likes wick and complex structure likes capillary are limited its popularization. Heat pipes are still under initial development.

3.2 Phase change materials (PCM)

PCM with a high energy storage density, high latent heats and excellent capabilities is another type of cooling material used in the BTMS. Large amounts of heat generated by batteries can be absorbed during the process of phase change so that maintain the temperature almost as a constant. The structure of the PCM cooling system is simple, the weight is light, and the temperature uniformity between the batteries is guaranteed.[22-24]

Based on their chemical properties, PCM can be divided into organic (such as paraffin and fatty acids), inorganic (such as hydrated salts), and eutectic materials (such as eutectic fatty acid mixtures along with hydrate salts).[25] Studies have shown that PCM can effectively improve the cooling performance by adding substances with high thermal conductivity and encapsulated metal additives[26], thereby improving safety of the LIBs.

Organic PCM have noncorrosive, non-toxic, congruent melting, chemical stability, almost no super cooling and so on.[27] One of the major drawbacks of organic PCM implementation is flammability. Palacios et al.[28] studied the thermal properties and the fire performance of flame-retardant organic PCM(Paraffin RT-21, and fatty acids mixtures of capric acid, myristic acid, and palmitic acid). It suggested that magnesium hydroxide and hydro magnesite strongly affect the melting enthalpy and tend to decrease the melting temperature. The addition of flame-retardant materials will decrease the flammability of bulk organic PCMs. Dheep et al.[29] studied the thermal reliability and corrosion characteristics of phenyl acetic acid organic PCM, and identified phenyl acetic acid was a promising PCM for solar space heating applications due to its good heat storage properties, long term thermal reliability and less corrosive characteristics.

The main advantages of inorganic PCM are high latent heat, relatively high thermal conductivity, non-toxicity, non-flammability and low cost, compared to organic PCM.[30] Zheng et al.[31] investigated two inorganic PCM salts $NaNO_3$ and eutectic $NaCl$-$MgCl_2$ by encapsulating in cylindrical steel capsules. The salts and the encapsulation methods chosen here can store thermal energy effectively with no discernible diminishment in storage capacity and sustained performance. Höhlein et al.[32] found inorganic PCM $MgCl_2 \cdot 6H_2O$ as a suitable cooling material alternative, this PCM has a melting temperature of 115.1±0.1°C and a phase change enthalpy of $166.9 \pm 1.2 J \cdot g^{-1}$, which can operate at phase change environment temperatures between 90 and 150°C.

Eutectics PCM are two or more soluble ingredients mixed, which have the feature of simultaneous melting and solidification without material's separation.[33] Mikhaylov et al.[34] synthesized an inorganic ZnO coating onto organically encapsulated paraffin PCM substrates based on hydrogen peroxide sol-gel processing, the differential scanning calorimeter(DSC) test showed an initial weight loss up to 300°C, which indicated it can perform normally even at a high temperature and good thermal stability. This is a way to benefit from the favorable attributes of both organic PCM and inorganic PCM with an improved thermal conductivity. Xu et al.[35] studied flame-retardant shape stabilized phase change materials(SSPCM) by coating acrylic resin/expandable graphite(EG), alkyd resin/EG and epoxy resin/EG. Vertical burning test showed no dripping occurs during combustion processes, because organic montmorillonite (OMMT) in the matrix increase the melt viscosity and the strength of strips, and suppress the evaporation of paraffin. EG in the coatings rapidly expanded like a “bread”, the expansion process was endothermic, and absorbed large amounts of heat. Thermogravimetric analysis(TGA) indicates those PCM could remain thermal stability beyond 200°C.

Attempts have made to improve the performance of PCM, more new methods and new materials are need to be developed and investigated for meeting the application requirements of future large-scale energy storage fields.

3.3 Fire extinguishing agents

Fire extinguishers likes carbon dioxide, heptafluoropropane, trifluoromethane, IG-541 (52% nitrogen, 40% argon and 8% carbon dioxide), hexafluoropropane, IG-100 (nitrogen), etc. were used with a mature technology and reasonably comprehensive performance index. Wang et al.[36] proved the feasibility of heptafluoropropane as a fire-extinguishing agent for batteries. The results show that heptafluoropropane can effectively extinguish fires of single or small batteries. Reports also shows that ABC dry powder, hydrofluorocarbons, water, perfluorohexanone and CO_2 fire extinguishers can quickly extinguish the open fire of batteries.

It should be noted that before the fire spread to a high voltage battery, CO_2 or ABC dry powder fire extinguisher could be used. Nevertheless, when flammable electrolyte vapor leak, an effective attempt is to cool the battery with the massive water of high pressure continually. Rechargeable LIBs were intercalated into graphite, lithium metal oxides, or lithium salts, making the lithium contained within these batteries inert to water [37]. However, pure metal lithium used in lithium-sulfur and lithium-air battery is explosively reactive with water. Furthermore, it can react with oxygen, carbon dioxide, and nitrogen in the air so that it can only extinguish fire by isolating air or flammable materials like sand and soil.

4. MATERIALS USED IN INTERNAL PROTECTION STRATEGIES FOR IMPROVING THERMAL STABILITY

4.1 Electrolyte

As a medium environment for lithium ion transport, conventional electrolytes are mainly composed of lithium hexafluorophosphate ($LiPF_6$) that dissolved in the mixtures of ethylene carbonate and linear carbonates, which were used as thinning solvents to improve the viscosity, wettability and conductivity as well as to suppress the crystallization of ethylene carbonate at low temperature. However, electrolyte, with a low flash point[about 25°C for the mixture of ethylene carbonate (EC)+dimethyl carbonate (DMC) electrolyte], is always considered to be closely related to its safety. In order to avoid various types of accidents caused by potential LIBs fire hazard, great efforts were made to optimize electrolyte flammability performance and improve the safety of LIBs. Flame-retardant electrolyte additives, ion liquid and solid-state electrolytes were performed to develop more thermal stability electrolytes.

4.1.1 Flame-retardant additives

Using flame-retardant additives in electrolyte is one of the most effective ways to improve the safety performance of LIBs. Flame-retardant additives effectively suppress additional fire spread in lithium ion battery for the non-flammable agent increases flash points of conventional electrolytes. It is well recognized that effective flame-retardant additives commonly used in electrolyte can be categorized into inorganic additives and organic additives.

4.1.1.1 Inorganic additives

The inorganic additive shows many excellent performances, such as high ionic conductivity[42, 43], non-flammability[43] and high lithium ion transport capacity.[44] Kinds of batteries, such as lithium-SO_2 rechargeable batteries[43, 45, 46], lithium-$CuCl_2$ rechargeable batteries [47] and lithium ion batteries [48, 49] are reported to have inorganic additives of flame-retardant. Both the electrochemical and thermal stability performances of these batteries are benefited from the excellent properties of inorganic additives.

The composite of inorganic additives in polymers electrolytes is another effective way to improve thermal resistance and flame-retardant properties.[50, 51] Kashiwagi et al.[52] indicated that the addition of inorganic additive silica acted as thermal insulation and barrier for the formation of strong char/silica surface layers so that protected the polyethylene oxide against the migration of thermal degradation products to the surface. They studied the flame-retardant performance of various types of silica/polyethylene oxide hybrids, all showed excellent thermal performance. In addition, introduction of nanocomposite in electrolyte is another effective means to improve the flammability resistance and the mechanical and electrochemical properties. Enotiadis et al.[53] synthesized well-dispersed nanocomposite electrolytes by leveraging the acid/base interactions of the surface hydroxyls on silica. The nanocomposite electrolytes decrease the rate of mass loss and heat release rate, and exhibit open-flame ignition resistance. Schaefer et al.[54], Jia et al.[55] and Lee et al.[56] reported a series of single-ion electrolytes based on lithium exchanged sulfonated silica nanoparticles by surface modification of the silica nanoparticles with sulfonated silane. Gao et al.[57] studied $LiAlCl_4 \cdot 3SO_2$ as a high conductive, non-flammable and inorganic nonaqueous liquid electrolyte for lithium ion batteries. Flammability tests showed a polypropylene separator that soaked with organic additive electrolyte(OE) burned immediately after exposure to an open flame. However, the glass fiber separator that soaked with inorganic additive electrolyte(IE) exhibited good flame-retardant and did not burn even after contacted with an open flame about few seconds. Compared with OE, $LiFePO_4$ cathode in IE exhibited outstanding rate capacity and stable cycle performance.

Inorganic additives, acting as solid plasticizers, enhance the segmental motion of the host polymer so that increase ion conduction of the electrolyte. Moreover, the nanocomposite electrolytes also suppress the amount of toxic gasses released during combustion by partially replacing toxic bis(trifluoromethane) sulfonimide lithium salt with inert lithiated silica.[53] Some of them or even have negative effects on battery performance. The flame-retardant effect is generally inferior to that of organic additives.

4.1.1.2 Organic additives

Organic phosphorous compounds, with various types, low toxicity, suitable physical characteristics, good compatibility and low cost[58], are the most effective flame-retardant materials. Currently, phosphate class compounds are mainly used as the flame-retardant molecules for electrolyte additives, which can efficiently block the chain reactions of hydroxyl radicals during the combustion of organic electrolytes solution.

For most of reported organic phosphorus additives materials, low molecular weight phosphates including trimethyl phosphate[59, 60], triethyl phosphate[60], dimethyl methyl phosphonate[61, 62], tributyl phosphate,[63] and diethyl ethylphosphonate[64], are promising non-flammable solvents.

Modifications organic electrolytes materials by using synergists, adjuvants and polymeric material additives were of great importance to flame-retardant performance. Wang et al.[65] developed a fire extinguishing organic electrolytes by using a salt and trimethyl phosphate. The trim ethyl phosphate based salt-concentrated electrolytes act as effective fire extinguishers, and no valid flash point up to their boiling points (beyond 200°C). Baginska et al.[66] developed core-shell microcapsules containing flame-retardant tris(2-chloroethyl phosphate) (TCP) for LIBs electrolyte, which prevented direct dissolution of the retardant agent into the electrolyte. The microcapsules are electrochemically stable and thermally stable to 200°C in the electrolyte. They also found that both TCP contents and capsuled TCP or not have influences on its charge capacity performance, 5wt% TCP microcapsule could afford a desirable thermal and electrochemical performance.

The alkyl phosphates additives have excellent flame-retardant ability for the high content of phosphorus reducing the self-heating rate.[67,68] But their high viscosity always cause low lithium ion migration rate and unsatisfactory electrochemical performance. Furthermore, this kind of additives materials will release corrosive, toxic gases and a large amount of smoke, which will cause air pollution and have a serious impact on human respiratory tract.

Researchers have made some modifications to use partial fluorination as alkyl phosphates electrolyte compounds. Halogen flame-retardant additives, which usually have a high flash point and good thermal stability, are used for battery electrolytes. By replacing organophosphorus additives with halogenated carbonates electrolytes, some of problem mentioned above can be solved and the flame-retardant performance of LIBs enhanced.

Organic fluoride additives with low viscosity, high solubility and good flame-retardant performance under low temperature help to reduce the attractiveness between solvent molecules and improve the conductivity.[69] Hydrofluoroether is a classical non-flammable liquid electrolyte component, many attempts coupled with it were to adapt their chemical properties to meet the criteria of battery electrolytes. Baik et al.[70] fabricated the polymer electrolyte by two-methyl carbonate modified on the terminal groups of perfluoropolyether chains. This gel polymer electrolyte represented wider operating temperature up to 175°C. Yokoyama et al.[71] pointed out that fluorinated cyclic carbonate esters have good physical and chemical stability, high flash point and dielectric constant. It can dissolve electrolyte lithium salts and miscible with other organic solvents. After amounts of additive adding, battery charge/discharge performance, cycle and flame-retardant performance have witnessed an increase compared to the original. Fan et al.[72] reported a non-flammable electrolyte consists of 1M $LiPF_6$ in a mixture of fluoroethylene carbonate/3,3,3-fluoroethylmethyl carbonate/1,1,2,2-tetrafluoroethyl-2′,2′,2′-trifluoroethyl ether(FEC:FEMC:HFE, 2:6:2 by weight). This all-fluorinated electrolyte enabled a high Li plating/stripping coulombic efficiency of 99.2% and showed excellent stability. Sato et al.[73] studied the application of methyl difluoroacetate and ethyl difluoroacetate fluorinated chain carbonates in battery electrolyte, it was found that these fluorinated esters not only had good high temperature stability, but also had low viscosity, low melting point and good low temperature performance. Smart et al.[74] reported that some fluorinated carbonates such as methyl-2,2,2-trifluoroethyl carbonate added to ternary or quaternary organic electrolytes can effectively reduce the flammability of electrolytes. Arai et al.[75] combined a proper proportion of methyl difluoroacetate with chain carbonate and chain ether. It was found that the flash point of electrolyte could be completely eliminated. There was no ignition in needling and overcharging tests, and the safety performance of batteries is good. Zhang et al.[76] found that about 15% tris (2,2,2-trifluoroethyl) phosphite (TTFP) fluorinated retardant additive could effectively make the $LiPF_6$ electrolyte non-flammable and increase ionic conductivity and cycling efficiency. They indicated that TTFP can suppress the PC decomposition and graphite exfoliation so that improve the high temperature (60°C) performance of the graphite/cathode Li-ion cells.

Moderate amounts of fluorinated retardants could be compatible well with $LiPF_6$ and improve the flame-retardant performance, but in a large dosage they show a poor compatibility and affect the battery performance. Therefore, it is of great importance to explore the appropriate lithium salt or modify the fluorinated retardant to improve the compatibility of $LiPF_6$ based electrolyte. The flame-retardant additives dissolved in the liquid electrolyte inevitably increase the viscosity of the electrolyte, leading to decrease in ionic conductivity, and decrease the power capacity of the battery. Besides, the cost of fluorinated additives materials is still very high at present, which requires special equipment and strict preparation processes. More improvements are needed to meet the flame-retardant performance and use safety.

4.1.2 Solid-state electrolytes

Solid electrolytes are a new class of solid-state ionic materials. LIBs with solid-state electrolytes were considered as one of the most important next generation technologies for large-scale energy storage battery systems. Since the solid-state electrolytes not only guarantee the transport of lithium ion but also acts as the battery separator during charging and discharging. The solid-state electrolytes will not leakage like liquid electrolyte so that avoid the side reaction with electrode materials and corrosion of the SEI, restrain the growth of metal dendrites, offer higher energy densities and thermal stability performance than the traditional batteries. They can be divided into solid-state polymer electrolytes, inorganic solid electrolytes and organic-inorganic hybrid composite electrolytes.

Ceramic solid electrolytes are well suited for high temperature applications for the high temperature resistance of ceramic materials. Murugan et al.[77] first reported the garnet-type $Li_7La_3Zr_2O_{12}$ ceramics as the solid-state electrolytes, which showed promising ionic conduction properties and thermal stability. Furusawa et al.[78] fabricated a metal silicate $Li_2O\text{-}SiO_2$ thin film on SiO_2 glass substrate by a pulsed laser deposition, while Wu et al.[79] synthesized titanates $Li_{2-2x}Mg_{2x}TiO_{3+x}$ ($0 \le 2x \le 0.1$) ceramic powder by solid state reaction, both of them have a high ionic conduction properties and thermal stability at higher temperatures than room temperature.

Several types of solid polymer electrolytes like poly (ethylene oxide), polycarbonate, polysiloxane, and plastic crystal have been developed. Porcarelli et al.[80] found a super soft all-ethylene oxide polymer electrolyte, which have outstanding cycling behavior in terms of rate capability and stability over a wide range of operating temperatures and a wide electrochemical stability window beyond 5V (vs. Li/Li^+). Such an electrolyte effectively resisted lithium dendrite nucleation and improved the interfacial stability. Zhang et al.[81] prepared a safety-reinforced poly(propylene carbonate) based all-solid-state polymer electrolyte, which exhibited superior electrochemistry performance at room temperature. When the temperature up to 120°C, cells using such solid polymer electrolyte can also operate normally. Zhou et al.[82] synthesized a hierarchical PVA-CN/SN solid electrolyte by in situ polymerizing the cyanoethyl polyvinyl alcohol (PVA-CN) in succinonitrile (SN)-based solid electrolyte in the network of electro spun fiber membrane. This solid electrolyte exhibits a distinctly low flammability that hardly ignited with the flame source. Attributing to the strong bond energy of C≡N bonds, it showed an excellent thermal stability that being negligibly volatile until a high temperature of 160 °C.

Organic-inorganic hybrid composite electrolytes are generally prepared by dispersing inorganic ceramic fillers (Al_2O_3, SiO_2, TiO_2, $BaTiO_3$, $PbTiO_3$, and $LiNbO_3$) and fast ionic conductors into organic polymer system. Here, the inorganic composites improve the high temperature resistance and mechanical properties while organic polymer composites act as the solvent, uniform dispersing in the inorganic composites and decreasing the interface impedance of electrolyte and electrodes. Xu et al.[83] synthesized a hierarchical nanoporous γ-Al_2O_3 encapsulated quasi solid electrolyte through a hydrothermal method, it exhibits remarkable thermal/mechanical stabilities and a broad electrochemical window up to 5.0V (vs. Li^+/Li). The SEM and HRTEM images show that the as-prepared γ-Al_2O_3 has a highly opened structure, with loose concentric nanosheets which consisted of highly orientated nano-fibers. Linear sweep voltammetry(LSV) and cycling curve shows an excellent electrochemical performance at the window up to 5.0V. Combustion test reveals that the solid-state electrolyte could be hardly ignited with one frame.

The biggest obstacle of solid electrolyte is that there may be a large contact resistance between electrodes and electrolytes, which affects the transport of lithium ions and increases heat generation. Therefore, more improvements are needed on the interface to meet the performance requirements of large-scale energy storage batteries.

4.1.3 Ionic liquids

The ionic liquid usually refers to the liquid salt at room temperature, which is obtained by dissolution of salts in molecular solvents. Such systems consist of solvated ions, their charged or neutral combinations and solvent molecules. Ionic liquids as a class of safe and green electrolytes have many desirable properties expected for lithium electrolyte, such as a long operation temperature range, low volatility and wide electrochemical window, low heat of reaction with active materials and non-flammability.[84] However, the common problems of ionic liquid are low conductivity under room temperature caused by high viscosity, lithium corrosion problem and high purity requirements limited by synthesis process.

During the last decade, an increasing number of new ionic liquids have been prepared and used as solvents. Guo et al.[85] fabricated an ionic liquid gel polymer electrolyte supporting by $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, which can not only effectively reduce the crystallinity of the polymer matrix, but also act as the lithium ion conductor, leading to higher ionic conductivity and lithium ion transference number. The membrane flammability tests show the ionic liquid gel polymer electrolyte supported by $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ even with the temperature maintained at 200 °C. Especially, the electrolyte shows good compatibility and no dendrite with Li metal anode, achieved good electrochemical performances and thermal safety. Damen et al.[86] reported a safe, innovative ionic liquid-based electrolyte N-butyl-N-methylpyrrolidiniumbis(trifluoromethanesulfonyl)imide($PYR_{14}TFSI$), which formed by N-n-butyl-N-methyl-pyrrolidinium cation [PYR^{14+}] and N,N-bis(trifluoromethanesulfonyl) imide anion [$TFSI^-$] with the lithium N,N-bis(trifluoromethanesulfonyl) imide (LiTFSI) as dissolved lithium salt. The test results show that the long cycling stability battery surpasses the energy and power goals stated by the United States Advanced Battery consortium (USABC) and Department of Energy, and this LIBs should be suitable for application in the evolving hybrid electric vehicle market. Lombardo et al.[87] studied the electrochemical properties of a ionic liquid-based electrolyte electrolytes by mixed commercial carbonate-based electrolytes with N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, the mixed electrolytes showed improvd electrochemical stability windows and a large reduction of the self-extinguish time when exposed to a free flame, and demonstrated the use of the mixed electrolytes in a complete device with a drastically improved safety profile. Chen et al.[88] demonstrated a novel heteroatom Si substituent imidazolium-based ionic liquid electrolyte, which showed a low viscosity of 73.5cP, ionic conductivity values exceeding $1.5 mS\cdot cm^{-1}$ at 25°C are obtained along with a wide electrochemical stability window of approximately 5V. This strategy of building heteroatom Si substituent ionic liquid is successful in reducing the viscosity, realizing safe and stable electrolyte for assembling a high-energy density battery.

4.2 Separator

Separator is a very important component to a battery. Even though the separator does not directly participate in the electrochemical reactions in a battery, it does significantly affect the cell performance of the battery as well as safety characteristics. If the separator is compromised, the battery may get into thermal runaway due to internal short circuit.[89] Though the cell temperature rises up, the separator must remain mechanically to separate the battery electrodes to prevent internal short circuits, and chemically stable to ensure the passage of lithium ions and good wettability with electrolytes.

Microporous polyolefin-based membranes consisting of polyethylene (PE) or polypropylene (PP) used to be the standard choice as separators for LIBs. They are easy to process and show decent mechanical and chemical stabilities at an acceptable cost.[90] However, these organic separators usually have low melting points (135 °C for PE and 165°C for PP), so that they could undergo obvious dimensional shrinkage even at the lower temperatures than their melting points, which may result in the direct contact of the anode and the cathode. Additionally, poor wettability of the polyolefin separators to electrolytes and high specific resistances are prohibitive for their use in high-power applications.[91]

It is desirable to develop new separators with good wettability and improved thermal stability to enable high performance with enhanced safety for LIBs. Some of them are modified based on traditional PP or PE separators, while others chose novel materials with an excellent high-temperature stability to prepare separators for LIBs.

Approaches like coating with inorganic micrometer-sized particles or with more temperature stable polymers were used to improve traditional polyolefin based separators toward high temperature stability. Others, using flame-retardant separators[92,93], detecting the dendrite via a smart separator for early warning [94], nonwoven mat separators,[95] and electrospinning fiber separators[96] were developed as efficient strategies for LIBs safety.

Separators based on conventional polymers like ceramic-coated separators display excellent thermal stability, negligible shrinkage at high temperatures and excellent electrolyte wettability due to the high thermos stability and hydrophilicity of ceramic materials.[97] A small amount of ceramic particles such as SiO_2 [98-100], Al_2O_3 [101,102] and TiO_2 [103] have been introduced to coat onto the surface of the polymer to obtain the ceramic coated separators. Shi et al.[103] compared the bare, IPTT-grafted, and TiO2-grafted PE separator before/after storage at 150°C for 0.5 h and found a TiO_2-grafted PE separator with an excellent thermal stability and electrochemical performances. Others, Yang et al.[104] demonstrated a core-shell structured SiO_2-polymethyl methacrylate (PMMA) sub-microspheres coated polyethylene separator. the FCC separator (12.9%) suppressed the thermal shrinkage to a markedly greater extent than the PE separator (31.4%) after being held at 130°C for 30 min. This improvement could be ascribed to the heat-resistant SiO_2 core particles. Lee et al.[105] developed a polydopamine (PDA)/Al_2O_3-coated PE separator, which retained their original size when exposed to temperatures of 145 °C over 30 min and maintained 94.8% (103.4 $mAh \cdot g^{-1}$) of the initial discharge capacity after 500 cycles at $C \cdot 2^{-1}$ rate and 51.7% (56.7 $mAh \cdot g^{-1}$) at 25 C rate. Lee et al.[106] introduced an Al_2O_3 ceramic coating layer on a PP-based microporous support, the Al_2O_3/PI-coated PP separators remarkably suppressed the internal short-circuit of the unit half-cells associated with separator thermal shrinkage(100 min at 160°C), it achieved an enhanced thermal stability and cell performances of the bare PP separators. Shi et al.[107] coated the porous PE membrane surface by Al_2O_3 ultrafine powder and thermal stable polyimide binder. This separator exhibits no thermal shrinkage up to 160°C and maintains stable when packed inner the cells up to 165°C. Li et al.[108] designed a high ion conductivity, high thermal stability and nonflammable shutdown PBI/PE/PBI sandwich-like composite membrane which exhibited no dimensional shrinkage up to 200°C. Hu et al.[109] compared a novel aramid nanofiber-coated PP separator with the pristine PP separators. These new membranes exhibited improved safety property of thermal stability up to 600°C.

Besides the modifications of traditional PP, PE separators, those membranes made only with more thermally stable polymers, such as polyacrylonitrile, polyimide, or melamine-resin, mostly in the shape of nanofibers, also show increased shrinking temperatures, high modulus and good battery performance. Zhang et al.[110] fabricated a composite membrane consisted of glass microfibers and polyimide, impressive improvement in thermo-stability and flame-retardant performance were achieved for the prepared composite membrane. Ji et al.[111] prepared ultra-strong polyoxyzole nanofiber membranes, which could operate at a temperature of 185°C. Hao et al.[112] synthesized flexible PBO-NMs by a highly scalable blade casting process, this membrane had decent liquid electrolyte wettability, low ionic resistance, superior thermal stability and with Young's moduli of 20 GPa and ultimate strengths of 525 MPa. Kim et al.[113] developed a c-mat separator consisted of a thin nanoporous TPY-CNF mat as the top layer and a thick macroporous electro spun PVP/PAN mat as the support layer, this separator showed a high-temperature cycling performance far beyond to commercial PP/PE/PP separator. Zhang et al.[114] developed a nanocomposite polymer membrane by introducing highly dispersed nano-TiO_2 hybrid doped poly(vinylidenefluoride-hexafluoro propylene)(PVDF-HFP) into a glass fiber nonwoven, which showed a higher thermal stability temperature and cycle stability than conventional PP separator.

4.3 Anode

Li metal, with characteristics of the highest specific capacity (3,862 mAh·g^{-1}) and the lowest potential of all, is optimal choice as an anode material.[115] Carbonaceous materials, especially graphite (specific capacity 372 mAh·g^{-1}), are the dominant commercial anode material for LIBs because of their low operating voltage, low cost and high abundance.[116] For anode materials, inhomogeneous lithium deposition on the lithium anode surface may form large dendrites and impale separator so that cause short circuit of the battery.[117] In addition, the thermal decomposition of the solid electrolyte interphase (SEI) is the most easily triggered chemical reaction between the anode and the electrolytes that pose the risk of overheating.[118] SEI deformation and continuously breaks enhances the interfacial resistance and leads to low coulomb efficiency. Therefore, to suppress lithium dendrite growth and to improve the thermal stability SEI are critical way to enhance the safety of the anodes.

The fundamental strategy to suppress Li dendrite is to avoid the Li dendrite nucleates or inhibiting the growth of Li dendrite crystal nucleus. Interface modification and structure manufactory are used to suppress the lithium dendrite growth. Xu et al.[115] indicated that anode were designed to 3D structure to slow down the orientation of free lithium crystals. In addition, using lithium powder anode effectively increased surface area and decreases the current density, which suppressed the formation and growth of dendrites. Zheng et al.[119] coated the lithium metal anode with a monolayer of interconnected amorphous hollow carbon nanospheres. A forming process of SEI layer before and after coating the hollow carbon nanospheres layer on the surface of deposited Li indicates many lithium ion deposition sites are provided. It helps isolate the lithium metal depositions and facilitates the formation of a stable solid electrolyte interphase thus avoiding the formation of sharp dendrites. Liu et al.[120] coating the lithium metal anode with a dynamically cross-linked polymer, the dynamic polymer can reversibly switch between its “liquid” and “solid” properties in response to the rate of lithium growth to provide uniform surface coverage and suppress dendrite. Wang et al.[121] coated the amorphous Li_3PO_4 thin films on the surface of Li metal foil via magnetron sputtering, the conformal coating layer Li_3PO_4 could successfully suppress the Li dendrite growth and improve its life span. Cheng et al.[122] proposed a sulfurized SEI by incorporating Li_2S into the interphase and eventually achieved uniform plating/stripping of the Li metal without Li dendrite formation.

As for SEI, its thermal stability could be improved by smoothing the active edge surfaces, removing some reactive sites or defects and forming a dense oxide layer on the anode material surface. Deposition of metals and metal oxides, doping with heteroatoms, coating with polymers and other kinds of carbons are general strategies reported.

Li et al.[123]designed an uniform Li_3PO_4 SEI layer by polyphosphoric acid (PPA) in situ reaction with Li metal and its native film. Test results in Li|$LiFePO_4$ battery systems indicated the artificial Li_3PO_4 SEI layer were stable in the electrolyte. Lithium metal depositions on the pristine film were disorderly while on the Li_3PO_4 SEI layer were homogeneous, which result in an improvement of the cyclic performance and charge and discharge capacity. Ma et al.[124] fabricated a Li_3N protection layer on the surface of a Li anode, which formed a stable SEI layer, prevented the side reaction of SEI and electrolyte, electrolyte and electrode and improved the safety of the battery. Huang et al.[125] reported a Li electrode connected in parallel with the lithiated graphite to modify the lithium metal anode. The self-regulated SEI layer effectively control the side reactions between anode and electrolyte, leading to significant performance and stability improvements. Zheng et al.[126] employed ionic liquid N-methyl-N butylpyrrolidinium bis(trifluoromethylsulfonyl)imide to modified the SEI layer, the ionic liquid enhanced passivation film on the lithium anode surface and exhibited very different morphology and chemical composition, which effectively protected lithium metal from continuous attacking. The irreversible consumption of polysulfide on lithium metal were reduced. This dense SEI layer effectively slowed down the rapid corrosion of lithium and the increase of the impedance.

4.4 Cathode

Layered oxides $LiCoO_2$, $LiNiO_2$, $LiMnO_2$ and ternary materials $Li(Ni_xCo_yMn_{1-x-y})O_2$ and $Li(Ni_xCo_yAl_{1-x-y})O_2$, the spinel-type oxide LiM_2O_4, and the polyanion type $LiFePO_4$, are popularly used cathode materials of LIBs. Cathode materials as an important active material in battery are required to intercalation and de-intercalation of lithium ions during charging and discharging, which must have an excellent thermal stability and an ability to prevent structural collapse. Among the decomposition temperature of those conventional LIBs cathode materials, $LiFePO_4$ displays the highest stable up to 310 °C, whereas $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiNi_xCo_yMn_zO_2$ and $LiMn_2O_4$ have an gradually increasing decomposition temperature of 150 °C [127], 160 °C [128,129], 210 °C [128] and 265 °C [130], respectively.

The major safety concern arises from the decomposition of these cathode materials at elevated temperatures and the simultaneous oxygen release, which together can lead to combustion and explosions that seriously compromise battery safety.[131-133] Considerable efforts have made to improve the thermal stability and safety of these cathode materials by surface protective coatings and atom doping.

Modification by coating is an important method to achieve improved cathode materials thermal stability. The coatings prevent the direct contact with the electrolyte solution and thus decrease side reactions and heat generation, suppress phase transition, improve the structural stability and decrease the disorder of cations in crystal sites. Materials used for surface modification include inorganic films, organic films, metal oxide, metal phosphate and metal fluoride, etc. Sun et al.[134] reported the improved cycling performance of ZnO-coated $LiNi_{0.5}Mn_{1.5}O_4$ electrodes at elevated temperatures from room temperature to 55°C. Wu et al.[135] synthesized layered $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ and $Li(Li_{0.1}Mn_{0.43}Ni_{0.23}Co_{0.23})O_2$ cathodes by modifying their surface with Al_2O_3, the surface-modified cathodes show significantly lower irreversible capacity loss and higher discharge capacity ($285mAh\cdot g^{-1}$) with excellent cycle ability compared to the unmodified counterparts ($255mAh\cdot g^{-1}$). Cho et al.[136] coated the $LiCoO_2$ cathode material with $AlPO_4$ nanoparticles, after the 12 V overcharge test, cell with bare cathodes exhibit short circuit and a rapid temperature increase to approximately 500°C, then burned and exploded. While for the cell with an $AlPO_4$ nanoparticle-coated $LiCoO_2$ cathode, the temperature only increased to approximately 60°C without burning, which indicated an $AlPO_4$ nanoparticle-coated can effectively improve the thermal stability of battery. Sun et al.[137] reported that AlF_3-coated $Li(Li_{0.19}Ni_{0.16}Co_{0.08}Mn_{0.57})O_2$ electrode greatly improved the electrochemical performance as well as the thermal stability. Stroeve et al.[138] found that the $LiMn_2O_4$ cathode modified by surface adsorption of poly(diallyldimethylammonium chloride) showed improved stability during charge/discharge cycling in organic electrolyte. Xia et al.[139] coated the $LiCoO_2$ cathode material by poly (3-decylthiophene) conductive polymer layer, which can transform rapidly to a highly resistive state so that shut down electrochemical reactions and side reactions once the temperature rises up to 80°C.

Atom doping is another strategy to improve thermal stability of the cathode material. Atom doping can cause materials lattice distortion and improve the stability of crystal structures, which significantly increase the thermal stability of the cathode materials. High-nickel $LiNiO_2$ as the most popular doping cathode material have derived $LiNi_xCo_{1-x}O_2$, $LiNi_xCo_yMn_{1-x-y}O_2$, $LiNi_xCo_yAl_{1-x-y}O_2$ and $LiNixMn_{1-x}O_2$ materials. Metal atoms (especially, transition metal atoms such as Co, Al, Mn, V, Ti etc.) doping in the cathode materials substantially enhance the structural reversibility and reduce the anisotropic lattice distortion upon cycling, both the thermal instability and electrochemical properties were found improving. Xie et al.[140] presented $Li_{0.98}Mg_{0.02}Ni_{0.94}Co_{0.06}O_2$ (NC-Mg) with 2% Mg doping, which significantly elevates the exothermic peak temperature of NC-Mg to 211°C, in sharp contrast to 177°C for NC. Both the DSC curve and electrochemical test results show an improved of thermal stable performance. Chen et al.[141] used the $LiNi_{0.8}Co_{0.2-x}Al_xO_2$ as cathode material by Al-doped $LiNi_{0.8}Co_{0.2}O_2$, it significantly stabilizes the cell impedance, decreases the heat produce in the process of charging and discharging and improves the safety of batteries.

5. CONCLUSION

With the development of energy technology, and increasing application trends of high energy, high power density battery, safety requirement of LIBs has become extremely important. In this article, recent key progress in materials for flame retarding and improving thermal stability of LIBs and the fundamental external and internal protection strategies for flame-retardant are reviewed. The flame-retardant performance of strategies related to the physicochemical properties of various kinds of materials.

For the external protection strategies, adopting advanced technologies, such as electronic devices temperature sensors and pressure valves to BTMS could detect and warn the characteristics information of battery behavior evolution. By combining with coolant materials, phase change materials and fire extinguishing agents, it can sufficiently suppress battery overheating, thermal propagation and burning. In addition, once fire or explode burst out, fire-extinguishing agent likes water, carbon dioxide or ABC dry powder fire extinguisher are directly used to suppress the thermal hazard propagation.

When it comes to the internal protection strategies, the mainly attention are focused on the thermal stability of individual component, including cathode materials, anode materials, separator materials and electrolytes based on material chemistry property. Many important methods to design thermal stability materials and improve safety of LIBs are introduced. Organic and inorganic flame-retardant electrolyte additives, solid-state electrolytes and ion liquid were performed to develop more thermal stability electrolytes. Various separators including ceramic-coated separators, nonwoven mat separators and electrospinning fiber separators were designed. Some of them were modified based on traditional PP or PE separators, while others chose novel materials with an excellent high-temperature stability. As for anode materials, interface modification and structure manufactory were used to avoid the Li dendrite nucleates or inhibiting the growth of Li dendrite crystal nucleus. Interface mild oxidation, deposition of metals and metal oxides, doping with heteroatoms, coating with polymers and other kinds of carbons to improve the thermal stability SEI are critical to enhance the safety. Atom doping and surface protective layer materials coatings are important method to improve the thermal stability of the cathode materials.

Category and performance of materials for flame retarding and improving thermal stability are various, and the same to protection strategies. However, only external protection cannot essentially solve the problem of thermal runaway of batteries, and only internal protection cannot early warn fire signals and flame-retardant. Therefore, the combination of internal and external protective strategies and adopting with proper flame-retardant materials is an effective method to improve safety of LIBs and has good application prospects in the future development of large-scale energy storage applications fields.

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