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Views & Comments

Battery Safety: From Lithium-Ion to Solid-State Batteries

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1. Introduction

To date, the application of lithium-ion batteries (LIBs) has been expanded from traditional consumer electronics to electric vehicles (EVs), energy storage, special fields, and other application scenarios. The production capacity of LIBs is increasing rapidly, from 26 GW·h in 2011 to 747 GW·h in 2020, 76% of which comes from China [1]. The performance of LIBs in terms of energy density, power density, safety, cost, and other aspects is also improving, so as to meet the stringent needs of different application scenarios. The rapid development of LIB technology and the continuous expansion of the market have put great pressure on battery safety, and broad attention from the public can be expected once a battery-related accident occurs. Battery-related accidents, especially in emerging applications such as EVs and energy storage, have been increasing in recent years. Moreover, the scale of such accidents increases significantly with the increase of battery capacity. The impact of battery-related accidents could seriously depress consumer confidence in the application of LIBs in certain fields. Therefore, it is essential to promote battery safety to enable the wider penetration of LIBs in various application fields and the sustainable development of the battery industry [2].

Researchers and engineers have proposed numerous methods to handle the safety issues of LIBs from the perspectives of intrinsic, passive, and active safety; among these methods, the development of solid-state batteries (SSBs) has great potential for covering all three types of safety strategies. SSBs employ more stable solid-state electrolytes to replace the volatile and flammable liquid electrolytes in traditional LIBs. Theoretically, the use of a solid-state electrolyte is expected to improve the battery's energy density and other performance indicators, while maintaining battery safety at a certain level [3]. Thus far, great efforts have been made to develop SSBs worldwide. Europe, Japan, the United States, and the Republic of Korea have launched national projects to support the research and development (R&D) of SSBs, including Battery 2030+ in Europe, RISING3 and Solid-EV in Japan, Battery500 in the United States, and K-Battery 2030 in the Republic of Korea. Different types of SSBs, such as sulfide-, oxide-, thin-film-, and polymer-based batteries, are being developed at the same time [3–6]. It is very important to strengthen both the fundamental scientific research and the applied research related to the safety of SSBs in order to facilitate the maturity of SSB technology and eventually establish a market. This paper will analyze LIB-related accidents that have taken place in recent years, describe the characteristics of these accidents, and discuss current strategies to improve the safety of LIBs. Furthermore, new opportunities for the use of SSBs in the design of a battery with intrinsic safety, passive safety, and active safety strategies at the material, cell, and system levels will be discussed.

2. A brief analysis of battery-related accidents

Taking EV batteries as an example, we analyze battery-related accidents in regard to the accident time, type of battery system, type of accident, and region. The basic information is summarized in Fig. 1.

(1) **Time:** Based on the number of relevant accidents over time, it is clear that battery-related accidents did not increase sharply with the rapid increase of EV ownership, indicating remarkable advances in battery technology and manufacturing quality levels. Most battery-related accidents occur in June, July, and August, indicating that high-temperature conditions are an important factor causing the deterioration of battery safety.

(2) **Battery system:** The proportion of LIBs using a cathode of $LiNi_xMn_yCo_zO_2$ ($x + y + z = 1$; NMC) in battery-related accidents is significantly higher than that of LIBs using a lithium iron phosphate ($LiFePO_4$, LFP) cathode, indicating that there is a statistical correlation between energy density and safety; that is, the higher the energy density of a battery, the higher its safety risk. This contradiction between energy density and safety in LIBs is because the chemistry is less stable when more energy is stored in the chemical bonds of electrode materials.

(3) **Accident type:** Battery-related accidents may occur during battery charging, car driving, battery abuse (e.g., a collision), or even when the battery is in a static state. Such accidents are rarely due to car collisions; in most of the accidents that are known to the public, smoke, flames, or explosions have occurred for no ostensible reason. This seemingly unpredictable feature, which differs from the safety-related behavior of traditional vehicles using a combustion engine, is referred to by the public as the so-called "spontaneous combustion of EVs," making consumers anxious about EV safety.

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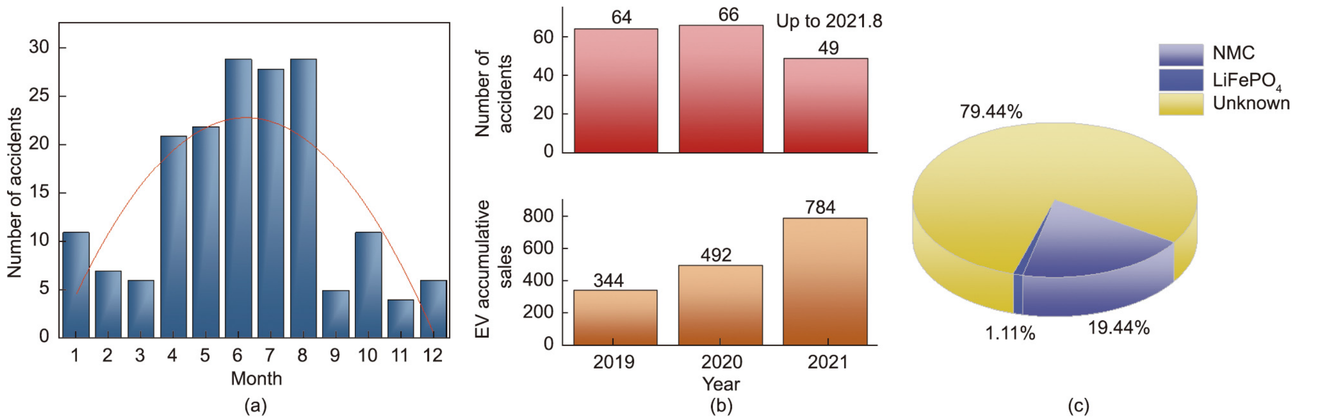

Fig. 1. Analysis of fire accidents involving EVs from January 2019 to August 2021. (a) Number of EV fire accidents monthly; (b) number of EV fire accidents and number of EVs yearly; (c) proportion of accidents caused by different types of LIBs.

(4) **Region:** Only following cities have reported more than three battery-related accidents: Hangzhou, Shenzhen, Xi'an, Shanghai, Beijing, Chongqing, and Wuhan. This is related to the big EV ownership in these cities.

Based on the above analysis, it can be found that: ① There is a certain probability of a battery-related accident occurring, which may be affected by various factors—such as the battery itself, the thermal management system, the charging device, and the operating environment—and in which a high-temperature environment plays a prominent role; ② the existence of "non-collision spontaneous combustion" depresses consumer confidence in EVs; and ③ among the reported data, the chance of an accident is greater for an NMC battery with a higher energy density than for a $LiFePO_4$ battery, indicating that a higher energy density worsens the battery safety.

3. State-of-the-art strategies to improve battery safety

At present, solutions for improving battery safety can be classified into the following three categories.

3.1. Improving the intrinsic safety of batteries

The intrinsic safety of the battery refers to the safety of the battery itself [7], which directly determines the probability of battery-related accidents. Many factors can affect the intrinsic safety of a battery, including the material used in the cell (i.e., NMC or LFP), cell design (i.e., thickness of the separator, the capacity ratio of the negative and positive electrode (N/P ratio)), manufacturing quality level (i.e., impurity control, fabrication accuracy), consistency, and reliability of the battery. The following strategies can be used to improve the intrinsic safety of a battery:

- **Improving the manufacturing quality level:** Good production and manufacturing quality are the foundation for battery safety. In past decades, rapid development has occurred in battery production technology and equipment. At present, the main battery manufacturers can control the product qualification ratio at a high level. The next generation of high-energy-density batteries has higher requirements for manufacturing. Therefore, intelligent manufacturing and Industry 4.0 are the focus of major battery manufacturers.
- **Improving the stability of battery materials:** Even if a high level of manufacturing quality is achieved, the intrinsic safety performance of an NMC battery with high energy density is obviously worse than that of an LFP battery, and it is still challenging to develop LIBs with both high energy density and high safety [8]. For high-energy-density batteries, the main solutions at the material and cell level are as follows: ① The surface coating, doping, composition, and structural design can be optimized to improve the structural stability of cathode materials at high temperatures. In recent years, coating the cathode surface with a solid–electrolyte that has a high ionic conductivity has received extensive attention, and has been shown to hold potential for solving the intrinsic oxygen-release problem of oxide cathode materials. ② A non-flammable solvent and a flame-retardant additive can be used to improve the thermal stability of the electrolyte and reduce the scale of thermal runaway. ③ The formation process can be controlled and an artificial solid–electrolyte interphase (SEI) can be designed to improve the thermal stability of the SEI thus increasing the durability of the battery at high temperatures. ④ New battery systems that theoretically have a higher level of safety can be developed, such as SSBs and aqueous batteries. However, the application of new technologies in the field of battery industry often takes years or even decades of time and effort, and these systems are still under development.

3.2. Passive strategies for battery safety

The main idea of passive safety is to keep the battery in a safe range at all times, and to control the influence of battery thermal runaway within a small range by means of redundancy design, without affecting the normal operation of the whole system. At present, passive safety is mainly achieved by thermal management of the battery system, which focuses on heat dissipation, heat preservation, and heat insulation [9].

- **Heat dissipation:** In order to ensure that the temperature of the battery does not exceed the upper limit of the normal operating temperature, the heat generated in the battery (especially during high-power operation) should be instantly dissipated. Air cooling and water cooling have been developed to replace natural cooling in the early stage and can greatly promote the cooling efficiency of the battery.
- **Heat preservation/preheating:** In addition to safety risks at high temperatures, lithium plating and local overcharge are critical issues when a battery operates at a low temperature, greatly reducing the intrinsic safety of batteries. Therefore, a battery needs to be preheated when it operates at low temperatures to ensure that the battery is above the critical temperature. At present, the main means of preheating is to heat the battery using a heating film installed at the bottom of the

battery pack. More efficient and less energy-consuming heating methods, such as battery self-heating, phase-change heating, or heat pump heating, are being developed.

- **Heat insulation:** Heat insulation is another important aspect of passive safety. The core idea of heat insulation is to reduce the impact of battery thermal runaway, prevent the thermal runaway of a single cell from causing heat spread, and prevent thermal runaway of the battery from further developing into the combustion and explosion of a battery system. At present, this is the most effective core means for EV enterprises to realize the lifelong non-combustion of EVs. Specific strategies include the use of heat insulation materials between cells, the design of a cellular structure, and a modular level of heat insulation. The ultimate goal is to ensure that the thermal runaway of a single cell cannot trigger thermal runaway propagation inside the battery system, resulting in an EV fire.

3.3. Active strategies for battery safety

The core idea of active safety is to monitor the characteristic signs related to safety concerns in the battery using built-in or external sensers and to issue a warning before the battery is about to lose control of heat so that the system stops working in time. Active security can be implemented with the help of big data and "small data." The idea of big data is to build a cloud platform, monitor the working status of each battery system in real time, and identify abnormal cells in advance. The main function of the currently used cloud platform is to identify deviations between the voltage of a single cell and the overall average voltage of all cells, so as to single out the abnormal cell and thus to issue an early warning. The most representative cloud platform in China is the National Monitoring and Management Platform for New Energy Vehicles built by the Beijing Institute of Technology, the framework of which was built based on the Shannon entropy algorithm [10].

However, due to the limitations of hardware and software, the data that the cloud platform can process is limited to voltage signals at present, and it is difficult to identify the changing rate of voltage signals due to the low real-time sampling rate (1 data per 30 s). Therefore, early warning is the main purpose of the big data platform. "Small data"—namely, the numerical values of the voltage, current, resistance, temperature, and signal change rate—plays a major role in the early-warning process. As thermal runaway is inevitably accompanied by characteristic reactions, certain characteristic parameters and their rate of change can be used as a warning of the occurrence of battery thermal runaway. The most typical parameters are temperature and voltage signals. When the temperature, voltage, and resistance of the battery are lower than the critical value, or when the change rate of these parameters is higher than the critical value, the battery system issues a thermal runaway alarm. Recently, studies have shown that the battery will release characteristic gases at the early stage of thermal runaway [11], so the content or change rate of these characteristic gases and the pressure inside the cell can be used as an alarm signal for battery thermal runaway. A good example is the hydrogen early-warning system developed by Zhengzhou University for energy storage power stations, which can warn about battery thermal runaway 10 min before the thermal runaway occurs [12].

4. Safety features of SSBs and opportunities for their use

The form of SSBs varies with their material system and cell design. SSBs are expected to greatly improve the intrinsic safety of the battery system and expand the design space for passive and active safety strategies. The SSBs under development can be divided into four types depending on the electrolyte they apply: namely, polymer-, thin-film-, sulfide-, and oxide-based SSBs. Their typical chemistry, characteristics, and improvement strategies are summarized in Fig. 2. The possible advantages of SSBs in improving battery safety will be discussed from the three aspects of the materials, cell, and system as shown in Fig. 3.

4.1. Materials level

4.1.1. Lowering the overall thermodynamic energy of the system

Because the thermodynamic stability of a solid electrolyte is higher than that of a liquid electrolyte, no violent chemical

Type	Chemistry	Characteristics	Developers	Improvement strategies
Polymer	Li PEO-LiFSI $LiFePO_4$, V_2O_5	● Easy to process ● Operates at 60–80 °C ● Prone to short-circuit ● < 4.0 V	SEEO, USA; Bollore, France	● Multi-layer separator ● Composite electrolyte ● Surface modification on electrode
Thin film	Li LiPON LCO, LNM	● Long cycle ● Adapts to high voltage cathode ● Low energy density ● High cost	Oak Ridge National Laboratory, USA; Sakit3, USA	● Roll-to-roll process ● Surface modification on electrode
Sulfide	Li, graphite ... LPS, LPSCl ... LCO, NMC ...	● High Li^+ conductivity ● High voltage cathode ● Contact deterioration ● Sensitive to air ● Hard for manufacturing	Toyota, Japan; Hitachi, Japan; Samsung, Republic of Korea; NIMTE, China ...	● Doping ● Composite electrolyte ● Liquid phase coating ● Surface modification ● Dry electrode process
Oxide	Li LLZO, NASICON ... $LiFePO_4$, LCO, NMC ...	● Stable at high voltage ● High thermal stability ● Prone to fracture ● High interface resistance ● Hard for manufacturing	Ohara, Japan; Mie Univ., Japan; Julich, Germany ...	● Composite electrolyte ● Gel interphase ● Solid electrolyte coating on cathode ● Amorphous oxide film

Fig. 2. Development progress of SSBs using different solid electrolytes. PEO-LiFSI: poly(ethylene oxide) dissolving $Li[N(SO_2F)_2]$; LiPON: lithium phosphorus oxynitride; LCO: $LiCoO_2$; LNM: $LiNi_{0.5}Mn_{1.5}O_4$; LPS: Li_3PS_4; LPSCl: Li_6PS_5Cl; LLZO: $Li_7La_3Zr_2O_{12}$; NASICON: sodium superionic conductor, including $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$; NIMTE: Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences; Julich: Julich Research Center.

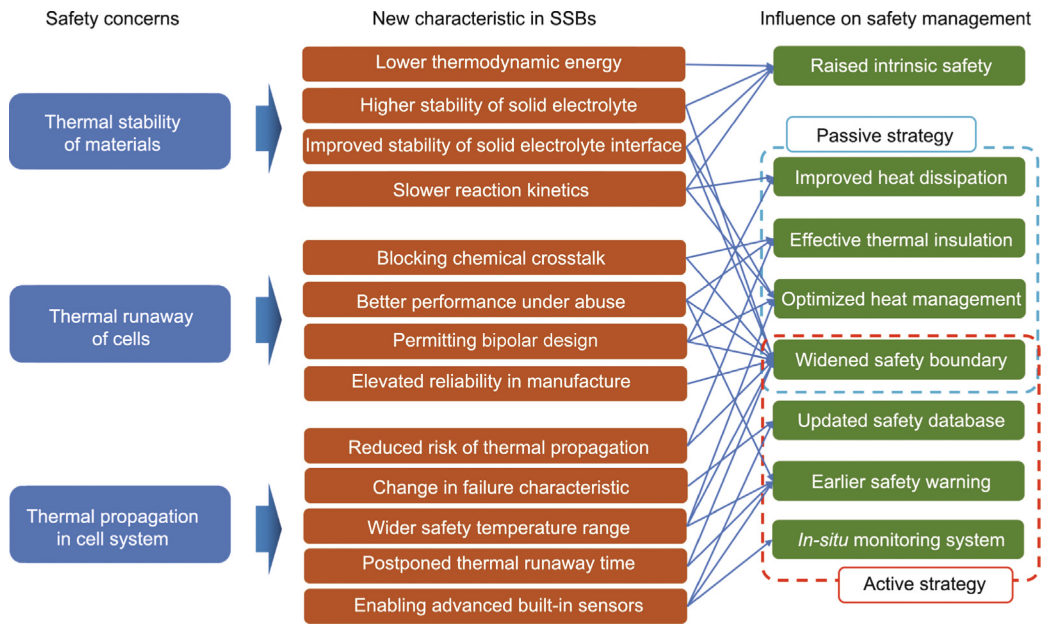

Fig. 3. Changes in material and battery design at the material, cell, and system levels provide new opportunities for battery safety design strategies for SSBs.

reaction can occur at high temperatures in an SSB. When other major components are the same and only the energy released by each component upon returning to the most stable state in the air is considered, an increase of solid electrolyte content and decrease of liquid electrolyte content will reduce the total energy released by the complete thermal runaway of the entire battery system and reduce the scale of the overall accident hazard.

4.1.2. Increasing the thermal stability

Since it is not likely that a solid electrolyte will participate in a combustion reaction, the stability of the interfaces in SSBs can be significantly improved [13], thus increasing both the spontaneous reaction and thermal runaway threshold temperatures, and broadening the safety boundary of SSBs. The main reason for the improvement of the stability of multiphase interfaces can be attributed to the stable SEI and cathode–solid-state electrolyte interphase (CEI) induced by a solid electrolyte coating or *in situ* formation which may delay the initial self-exothermic temperature of the battery [14]. For all-solid-state batteries (ASSBs), the electrode and electrolyte interface may have even higher thermal stability. As demonstrated by recent study by Chen et al. [15], even for a lithium metal anode, the initial reaction temperature between the oxide electrolyte and the lithium anode is higher than 250 °C, which is much higher than that between a liquid electrolyte and a lithium anode (generally 60–120 °C). This finding indicates that, although thermal runaway may not be completely avoidable at high temperatures, lithium metal has a better safety performance in SSBs than in liquid LIBs.

4.1.3. Postponing the reaction kinetics

Since most solid electrolytes are stable with a lithium anode, reactions between the electrode and a solid electrolyte will not continue to occur, even if the SEI has been decomposed. Moreover, a solid electrolyte coating on the electrode material may also prevent spontaneous surface reactions. In addition, recent studies have shown that solid electrolytes in SSBs may slow down the reaction of electrode materials and electrolytes [16], which may delay the temperature increase of the battery system, avoid the acceleration of exothermic reactions to thermal runaway, and provide a longer response time for a battery safety warning.

4.2. Cell level

4.2.1. Blocking the chemical crosstalk between the cathode and anode

Since solid electrolytes can be dense, it is possible to delay or block the diffusion of oxygen released from the cathode electrode or of hydrogen produced from the anode electrode by means of rational cell design, so as to avoid chemical crosstalk inside the battery and improve the intrinsic safety characteristics of SSBs.

4.2.2. Improving the durability against thermal abuse

Building on the abovementioned analysis of the material level, the introduction of solid electrolytes can effectively improve the ability of SSBs to withstand thermal abuse, and it is expected that the safe temperature for the hot-box test can exceed 200 °C. The wider electrochemical stability window of solid electrolytes is beneficial for improving electric abuse-resistance characteristics. Due to the high strength of the separator (a solid electrolyte or a separator coated with solid electrolyte), significant internal short-circuits can be avoided and mechanical abuse-resistance characteristics can be improved when mechanical damage occurs in batteries. In addition, the high stability of solid electrolytes against lithium metal can effectively reduce the risk of lithium plating during fast charging, which can lead to the severe thermal runaway of LIBs using a liquid electrolyte [17].

4.2.3. Enabling the "bipolar" design

Bipolar designs require limited mobility of the electrolyte in order to avoid self-discharge; therefore, they can only be realized in SSBs. Bipolar batteries may have better safety because they produce less heat during operation, reducing the pressure imposed on the thermal management system and facilitating the design of larger cells. In addition, the cells are assembled in series in a bipolar battery, so the safety risk can be greatly reduced when an SSB encounters electrical and mechanical abuse, such as fast charging and collision-incurred short-circuits [18].

4.2.4. Increasing manufacturing reliability

As SSBs have higher overall electrical, thermal, and mechanical strength, they have a higher safety tolerance to electrode degradation, overcharge and over-discharge, the generation of lithium metal dendrites, and short-circuits caused by impurities, which may reduce the risk of accidents caused by manufacturing defects in batteries and improve manufacturing reliability.

4.3. System level

4.3.1. Reducing thermal runaway spread in the battery system

Because SSBs contain no or a limited amount of liquid electrolyte, large amounts of combustible gases are not generated in the battery system, making it possible to avoid external combustion and reduce the risk of heat spread in battery thermal runaway. Moreover, the relatively slow and low heat production by SSBs is conducive to preventing thermal runaway propagation between cells and effectively ensuring the overall safety of the battery system.

4.3.2. Passive security: Increasing thermal management redundancy

Due to the higher thermodynamical stability of SSBs, the safe operating temperature range of the system can be extended. Furthermore, the interface side-reaction self-release heat may decrease, and a bipolar battery design can reduce heat production in the battery system, making it easier to achieve efficient heat dissipation. In addition, since flammable gas spills cannot occur, it is expected that the efficiency of the insulation design and system integrity can be improved.

4.3.3. Active security: Extending the early-warning time

Due to the lower heating rate of thermal failure of SSBs, the battery system may experience a longer time from the occurrence of an abnormal status and the detection of abnormal temperature, voltage, and mechanics signals to complete thermal runaway, so the early-warning system may have a longer response time.

4.3.4. Active security: Enabling an advanced senser warning system

Built-in sensers are not favorable for liquid LIBs, because liquid organic electrolytes are generally corrosive to sensers. This problem will be solved in SSBs, allowing the realization of lifelong high-precision *in situ* condition monitoring of the battery system.

5. Conclusions

In summary, although LIB technology is making continuous progress and the application of various safety strategies is significantly improving battery safety and reliability, liquid electrolytes are still a bottleneck in further elevating the energy density and safety of LIBs. Theoretically, SSBs have the potential to significantly improve intrinsic safety, thereby reducing the need for passive safety and active safety measures, as shown in Fig. 4. With advanced bipolar cell design and the employment of a lithium metal anode, SSBs are a feasible technological route to achieve both high energy density and high safety. Currently, the conductivity of solid electrolytes can meet the basic requirement for battery applications. The key bottlenecks are the stability of the solid electrolyte and electrode interface in many aspects (i.e., chemical, electrochemical, and mechanical), and the overall manufacturing of the battery, where a great breakthrough is still needed. One possible route is a gradual transition from LIBs to SSBs by gradually reducing the proportion of liquid electrolytes in the battery (i.e., hybrid solid–liquid batteries via *in situ* polymerization) and eventually ending up with ASSBs. The feasibility of this technical route has been partially verified; for example, mass production of hybrid solid–liquid batteries (360 $W\cdot h\cdot kg^{-1}$) has been successfully achieved by Beijing WeLion New Energy Technology Co., Ltd., and the batteries will be installed in EVs by the end of the year. However, as various technical routes are still competing, comprehensive research must be performed to study the safety failure behavior and mechanism, so as to determine a practical technical route for SSBs, accumulate sufficient scientific knowledge in the early stage of real mass production, determine the safety characteristics, and design corresponding protection and early-warning measures, which will help to promote the rapid application of SSBs.

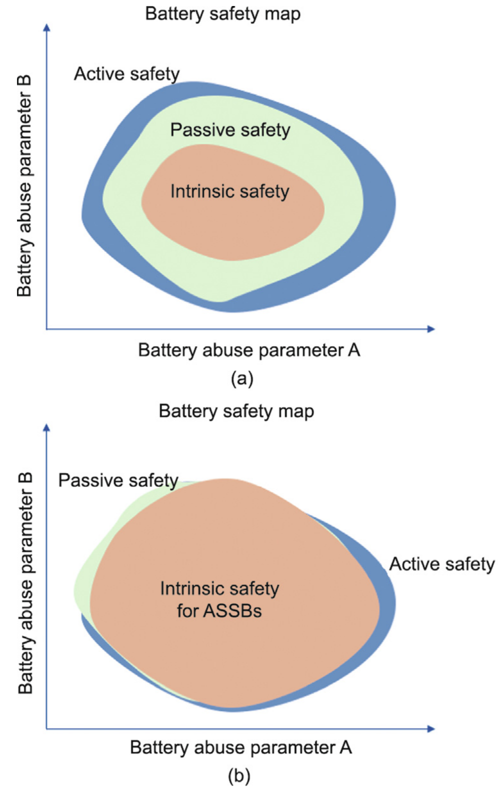

Fig. 4. Changes in the intrinsic safety, passive safety, and active safety when moving from (a) LIBs to (b) SSBs.

Acknowledgments

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