

Perspective

Mitigating Thermal Runaway of Lithium-Ion Batteries

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This paper summarizes the mitigation strategies for the thermal runaway of lithium-ion batteries. The mitigation strategies function at the material level, cell level, and system level. A time-sequence map with states and flows that describe the evolution of the physical and/or chemical processes has been proposed to interpret the mechanisms, both at the cell level and at the system level. At the cell level, the time-sequence map helps clarify the relationship between thermal runaway and fire. At the system level, the time-sequence map depicts the relationship between the expected thermal runaway propagation and the undesired fire pathway. Mitigation strategies are fulfilled by cutting off a specific transformation flow between the states in the time sequence map. The abuse conditions that may trigger thermal runaway are also summarized for the complete protection of lithium-ion batteries. This perspective provides directions for guaranteeing the safety of lithium-ion batteries for electrical energy storage applications in the future.

INTRODUCTION

The world is becoming increasingly electrified. Mobile electronics,¹ transportation,² and stationary energy storage³ are calling for better batteries. Lithium-ion batteries (LIBs) win over others because of their high energy density and long cycle life. To develop better LIBs, the safety problem, known as “thermal runaway (TR),”⁴ must be overcome. Solutions to this problem are urgently required to pass the last mile for the application of high-energy LIBs; fortunately, there are several techniques that can help mitigate battery TR. A mitigation technique can function before, during, or after the triggering of TR, according to the timeline of the accident.⁵ Effective mitigation techniques can be realized by design, monitoring, and active control. Moreover, the mitigation technique should be able to function at the material level, cell level, module level, or system level. Importantly, good mitigation techniques always function according to the underlying mechanisms. This perspective summarizes the current-best knowledge of the TR of LIBs. It not only covers the comments in current literature but also suggests solutions to the TR problems of LIBs and points out the areas that should be further investigated.

COMMON CHARACTERISTICS OF BATTERY THERMAL RUNAWAY

Figure 1 shows a common failure sequence in a battery system. TR is always triggered by various kinds of abuse, including mechanical abuse, electrical abuse, and thermal abuse. A latent defect may also evolve into a triggering factor during the cycle life. The TR of LIBs usually occurs with smoke, fire, or explosion during the process of intense energy release. TR propagates from one initiating cell to its neighbors and can cause disastrous consequences at the system level. Herein, we focus on TR mitigation strategies as our core information. Figures 2 and 3 show the TR mechanisms at the cell level and propose effective mitigation strategies according to the mechanisms. Figure 4 shows the mechanisms of TR propagation and proposes correlated

Context & Scale

Ensuring safety is the utmost priority in the applications of lithium-ion batteries in electrical energy storage systems. Frequent accidents with unclear failure mechanisms undermine the confidence of the industry in utilizing lithium-ion batteries. Moreover, lithium-ion batteries have a unique failure problem, named “thermal runaway,” of which the mechanism is still unclear. Thermal runaway is associated with chemical reactions, short circuits, smoke, fire, and explosion, making the situation more complicated than we can imagine. The real process that drives the failure hides behind deceptive observations. This perspective proposes mitigation strategies for the thermal runaway problem of lithium-ion batteries. The thermal runaway mechanism has been investigated using a time sequence map to the best of our knowledge. The state transition in the time sequence map clearly interprets the underlying mechanisms for all kinds of observations in thermal runaway tests. Effective mitigation strategies have been proposed based on the conscious understanding of the thermal runaway mechanisms. Fortunately, we can properly regulate the thermal runaway hazard and significantly reduce





Figure 1. The Failure Sequence of Thermal Runaway in a Battery System

From left to right, (1) the failure or thermal runaway can be triggered by electrical abuse, mechanical abuse, or thermal abuse. Latent defect inside the cell may evolve into severe hazard after long-term incubation. (2) The occurrence of thermal runaway at the cell level. (3) The failure propagation from one cell to its neighbors, from cell to module, from module to module, and from module to pack.

mitigation strategies at the system level. Figure 5 presents the abuse conditions of the LIB system and correlated mitigation strategies. The aim of TR mitigation is to enhance the thermal stability of LIBs, thereby reducing the consequent thermal hazard. Although there might be other factors that can induce safety issues, the thermal stability is what we concentrate on, because battery failure always results in temperature rise. The quantified characteristics of battery TR are essential for developing effective mitigation strategies. We recommend accelerating rate calorimetry (ARC) as a proper technique for TR analysis because it can provide an adiabatic test environment that focuses on measuring heat generation and excludes the influence of heat dissipation to the environment. The heat dissipation effect at the system level is shown in Figure 4. The repeatability of the ARC test is much better than those of other test methods. Figure 2 briefly shows the procedure of an ARC test. The cell sample is placed inside the ARC chamber, where it is heated to the point of TR. The heating process conforms to a standard process named “heat-wait-seek.” The ARC system will follow the temperature of the test sample to provide an adiabatic test environment, called the “exotherm” mode, once it detects noticeable heat generation from the test sample. The ARC monitoring system records the signals, e.g., temperature and voltage, which are further used for analyzing the TR mechanisms.⁶ We have summarized the common characteristics of battery TR after reviewing the results of many battery samples.⁷ $\{T_1, T_2, T_3\}$ and the $\max\{dT \cdot dt^{-1}\}$ are the common characteristics of battery TR. T_1 represents the onset temperature of abnormal heat generation, i.e., the moment at which the ARC system detects noticeable heat generation from the side reactions within the cell. T_1 reflects the overall thermal stability of a battery cell. T_2 is the triggering temperature of the battery TR. T_2 is the tipping point that separates the gradual temperature increase from the sharp temperature increase. The temperature increase rate, $dT \cdot dt^{-1}$, will change by several orders of magnitude after reaching T_2 . T_3 is the maximum temperature during TR. The $\max\{dT \cdot dt^{-1}\}$ reflects the maximum heat release rate during TR, with positive correlations with the energy density of the cell sample.⁷ The mitigation target of the battery TR is to increase T_1 and T_2 , and decrease T_3 and $\max\{dT \cdot dt^{-1}\}$.

MITIGATING THE THERMAL RUNAWAY HAZARD AT THE CELL LEVEL

The accurate control of the TR hazard relies on having an in-depth knowledge of the formation of the characteristic temperatures $\{T_1, T_2, T_3\}$. We have already acquired

the possibility of battery failure using the proposed control strategies, which can function at the material, cell, or system level in practical situations.

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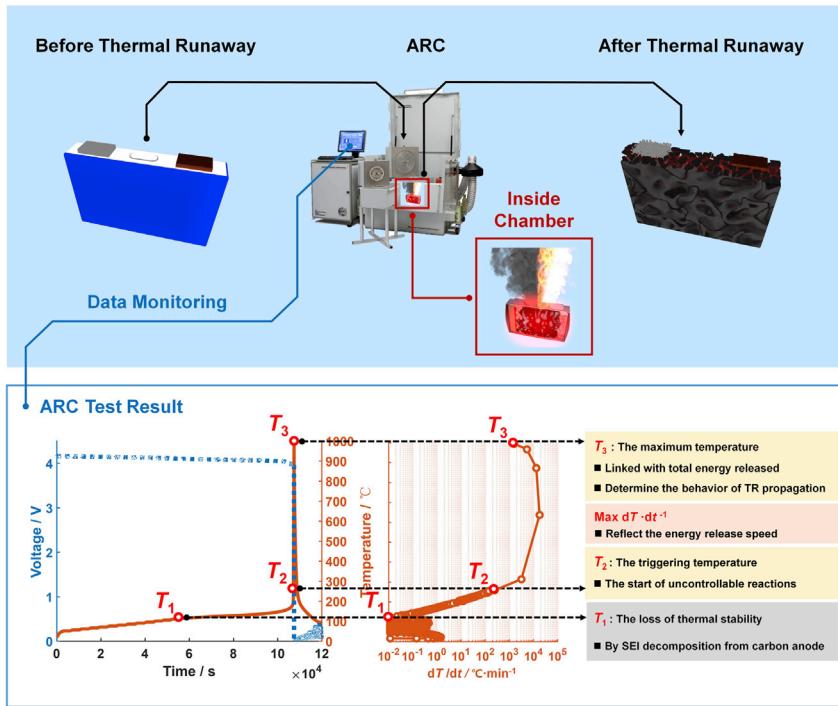


Figure 2. Common Characteristics of the Thermal Runaway of LIBs

ARC provides adiabatic test conditions that help to acquire repeatable results of thermal runaway for LIBs. The cell sample is placed inside the chamber that heats the battery to thermal runaway. The monitoring system of ARC records temperature, temperature rate, and voltage during thermal runaway. Three characteristic temperatures { T_1 , T_2 , T_3 } are regarded as the most important features of battery thermal runaway. T_1 represents the loss of thermal stability, T_2 denotes the triggering temperature, and T_3 is the maximum temperature that a cell can reach during thermal runaway. The maximum $dT\cdot dt^{-1}$ reflects the maximum heat release rate during thermal runaway.

detailed knowledge of the mechanism of battery TR.^{8,9} In 2018, we proposed the time sequence map (TSM) as a new approach to revealing the TR mechanisms for different kinds of LIBs.¹⁰ The TSM narrates the TR process through timelines. The concept of a thermodynamic system helps to categorize the individual physical and/or chemical processes according to the locations where they occur. The physical and/or chemical processes can occur inside or outside the cell case; therefore, we can redraw the TSM using the two-path pattern, as shown in Figure 3. Figure 3A outlines the two-path pattern for interpreting the TR mechanism of LIBs. The IN path represents the thermal failure caused by the chemical reactions inside the cell, whereas the OUT path is for the smoke, fire, or explosion outside the cell. TR mitigation is achieved by regulating the time sequence through the pathways. First, we need to prepare the map for physical and/or chemical processes during TR and subsequently propose regulating approaches to mitigate the TR hazards at specific points. The region with warm colors in Figure 3B shows a detailed TSM for the TR of LIBs. The IN path grows from the bottom-up on the left side, showing the sequence of thermal failure inside the cell case. The OUT path grows on the right side, showing the sequence of vent, smoke, and fire observed outside the cell case. The IN path determines the temperature rise of the cell, explaining the formation mechanisms of { T_1 , T_2 , T_3 }. The IN path includes the isolated reactions at the cathode or anode, the redox reactions between the cathode and anode, and the internal short circuit. The OUT path depicts the smoke, fire, or explosion that can be observed from outside the cell case. The moment of rupture is crucial for the

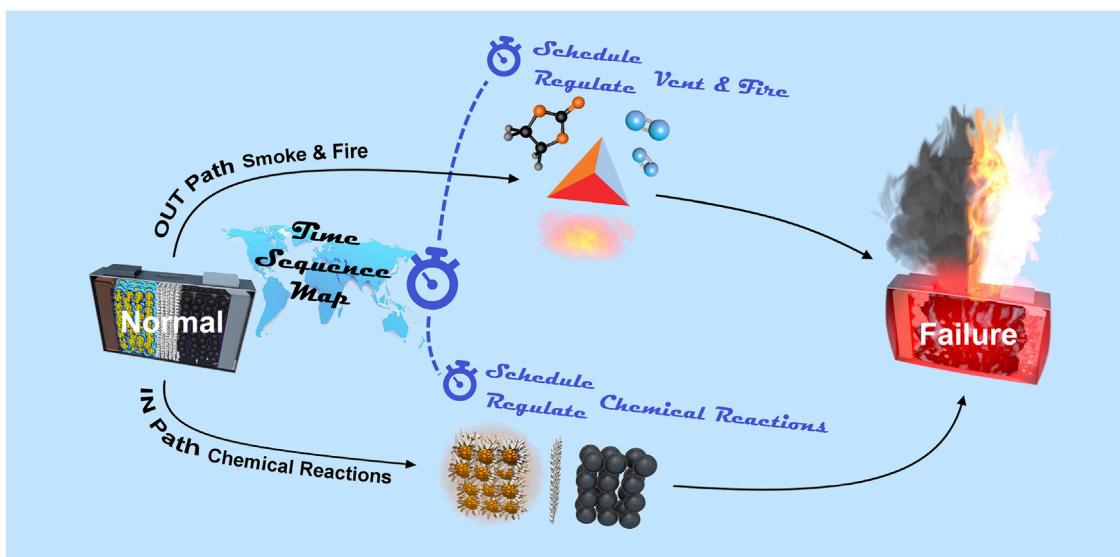
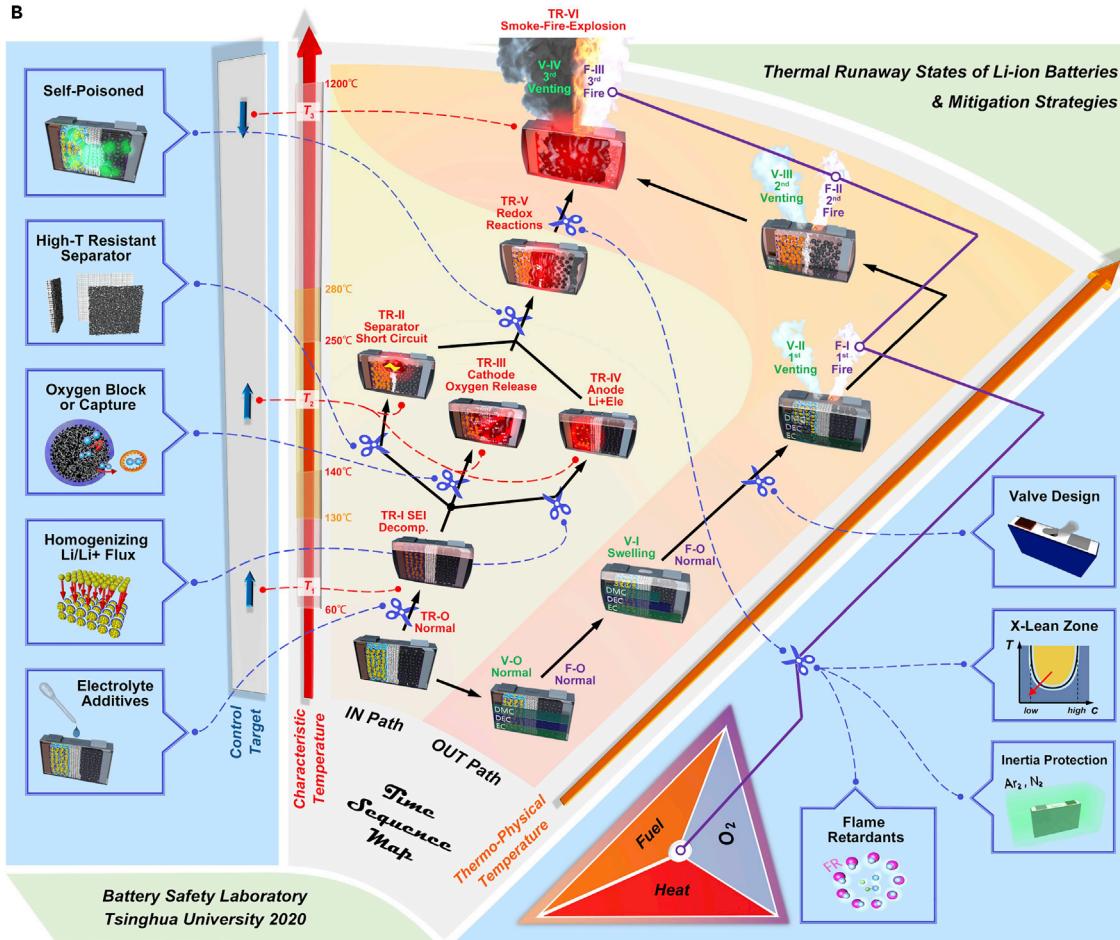
A**B**

Figure 3. Thermal Runaway States of LIB Cell and Correlated Mitigation Strategies

(A) An outline of the battery thermal runaway mechanisms and the thought of time sequence regulation. A cell can transit from normal condition to failure condition through two paths. The IN path is for the thermal failure caused by chemical reactions inside the cell, whereas the OUT path is for the smoke, fire, or explosion outside the cell. A proposed idea to mitigate battery thermal runaway is to schedule and regulate the time sequence of the dual paths.

(B) A detailed figure of Figure 3A. The vertical axis (in red) links with the characteristic temperatures as defined in Figure 2. The lean axis (in orange) links with the thermo-physical temperatures of the solvent with multiple components. Each node (a prismatic battery cell) that locates within the sector represents a unique state (check Table 1 for details if interested) during the thermal runaway process. The left path (IN path) shows the sequence of thermal failure inside the cell case until thermal runaway occurs. The right path (OUT path) shows the sequence of vent, smoke, and fire observed outside the cell case, of which the observation can be explained by the fire triangle. The code that sits on the shoulder of node denotes the name of the state. The prefix TR means the thermal runaway within the cell case, V means venting, and F means fire. The arrows between nodes refer to the state transitions, some of which can be cut off by proper mitigation strategies. The red dotted lines link the underlying mechanisms with the measured characteristic temperatures $\{T_1, T_2, T_3\}$. The mitigation target is to increase T_1 and T_2 and decrease T_3 . The blue scissors denote the critical points where we can cut off the paths before thermal runaway. The blue dotted lines link the specific mitigation methods (on the side of the figure) with the cutoff point where they function.

development of the OUT path. The rupture, which is mainly caused by electrolyte leakage, is the essential condition required for smoke, fire, and explosion.

The IN path summarizes the physical and/or chemical processes inside the cell from the ambient temperature to the TR orderly. T_1 is formed when the solid electrolyte interphase (SEI) starts to decompose.⁷ Usually, the SEI decomposition and regeneration drive the temperature from T_1 to T_2 for lithium-ion cells with a graphite anode. The formation of T_2 can be explained by the "cask effect," i.e., the weakest among the cathode, anode, and separator determines the formation of T_2 . As we already know, the main heat released during TR comes from the redox reactions between the cathode and anode (the state TR-V in Figure 3B); the specific process at T_2 acts similar to a detonator that triggers the main reaction. To date, the known detonators include (1) the internal short circuit caused by the collapse of the separator,⁷ (2) the highly reactive oxygen released from the $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathode,¹¹ and (3) the plated active lithium on the anode surface caused by improper charging.¹² At this point, we believe it might be essential to explain the new interpretation of the formation of T_2 . Previously, it was believed that the TR is always detonated by the internal short circuit. This is not wrong, because, previously, the triggering temperature of the states TR-III (for the cathode) and TR-IV (for the anode) (shown in Figure 3B) was considerably higher than that of the internal short circuit (TR-II in Figure 3B). In recent years, as the collapse temperature of the separator significantly increases while the utilization rate and the energy density of the cathode and the anode are further exploited by the industry, we gradually see the "trident" of the TR detonator, as shown in Figure 3B. Extreme fast charging that may feed a battery within 15 min may lead to the massive lithium plating. T_1 will significantly reduce to 60°C or lower,¹³ once a large amount of lithium is plated on the anode surface. Some of the recent accidents have indicated that the cause is likely the lithium plating under fast charging. This reminds us of the E-One Moli's tragedy in the 1980s. The performance of lithium-ion cells with the anode surface covered by plated lithium can have similar characteristics as that of lithium cells. Conversely, the utilization of a high-nickel-content cathode greatly reduces the temperature of the released oxygen.¹⁴ The industry should be aware of the "TR-trident," as shown in Figure 3B, despite considering that more time is required for previous knowledge to pass on. Finally, the redox reactions between T_2 and T_3 also generate a large amount of gases. The gases burst out with the active materials coated on the current collectors, because the aluminum current collector may melt at 660°C.

The OUT path summarizes the phenomenon, e.g., swell, rupture, smoke, fire, or explosion, which can be observed during the TR tests. The cell rupture, which is critical

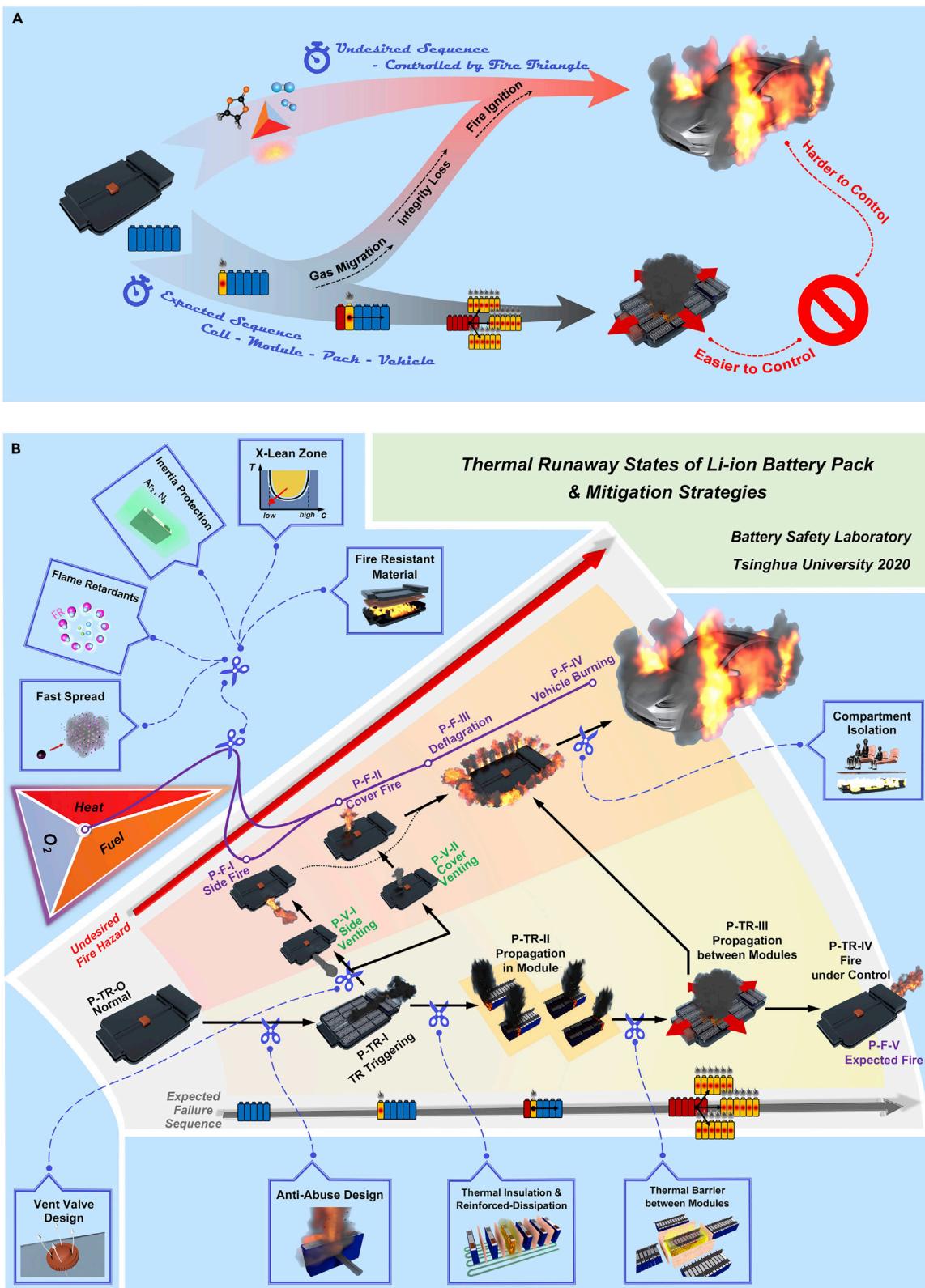


Figure 4. Thermal Runaway States of LIB Pack and Correlated Mitigation Strategies

(A) An outline of the battery thermal runaway propagation mechanisms and the thought of time sequence regulation. Two paths connect the normal condition and the disastrous failure. One path is for the thermal propagation mainly controlled by heat transfer, whereas another path is for the fire propagation controlled by the fire triangle. Path transition is possible when gas migration, integrity loss, and fire ignition are triggered. The lower path is relatively easier to control than the upper path. Therefore, we call the lower path as "expected," whereas we call the upper path "undesired." (B) A detailed figure of Figure 4A. The horizontal axis (in gray) refers to the expected failure sequence, which is considered during the safety design of battery pack. The lean axis (in orange) refers to the undesired fire hazard during the failure propagation within a battery pack. Each node (a battery pack or module) that locates within the sector represents a unique state during the thermal runaway propagation process. The horizontal path shows the expected sequence of thermal runaway propagation, which initiates from cell, propagates to the module, and finally spreads to the whole battery pack. The upper path shows the undesired fire hazard that may occur at pack level, of which the mechanism can be explained by the fire triangle. The upper path is also connected by the flow (purple line) originated from the fire triangle. The code on the shoulder of the node denotes the name of the state. In addition to the prefix in Figure 3, the additional prefix P means the state is for the pack level. The arrows between nodes refer to the state transitions, some of which can be cut off by proper mitigation strategies. The blue scissors denote the critical points where we can cut off the paths toward more severe hazards at pack level. The blue dotted lines link the specific mitigation methods (on the blue region at the side of the figure) with the cutoff point at which they function.

for the OUT path, occurs when the inner pressure exceeds the preset open pressure of the vent valve. The gas that accumulates inside the cell is generated from two sources: (1) the gasification of carbonate solvents and (2) the side reactions. A recent study¹⁵ and our results indicate that the gasification of solvents is the major source of gas before T_2 is reached, whereas the second gas source, the side reactions, will dominate the first source of gas after T_2 is reached. The internal pressure of the battery cell will increase when the temperature exceeds the boiling point of any of the components in the binary or ternary solvents. It is easy for the vaporized solvents to erupt and be exhausted from a pouch cell (usually without a vent valve) once the internal pressure increases. A hard-case cell with a vent valve can hold for a while until the inner pressure exceeds the opening pressure. Therefore, the rupture temperature for the pouch cells will be near the boiling point of the carbonate that vaporizes first, whereas that for the hard-case cells will be higher. The battery cell swells (the state V-I/F-I in Figure 3B) before the gas is exhausted. The fire triangle might be satisfied once the flammable gas vents from the cell package. Thus far, an observant reader may have realized that there might be no close relationship between TR and fire. The evolving paths of the TR and fire move forward in parallel conditions as in Figure 3B. However, in fact, it is the TR that generates a large amount of heat, which is one of the three factors in the fire triangle; it is the temperature rise owing to TR that stimulates the rupture of the cell, and it is the sparks generated during the high-speed venting that ignite the flammable gases. TR is the root cause of smoke, fire, and explosion for LIBs. It is worth mentioning that the oxygen released from the cathode is insufficient for the complete combustion of the flammable electrolytes,⁵ therefore, combustion will not occur inside the battery cell during the TR process.

The OUT path can help explain the mechanisms of the observations in the failure tests. Multi-stage jet fires have been observed in recent researches,¹⁶ and they can be attributed to the multi-stage venting of individual components of solvents, as the electrolyte of commercial LIBs usually contains two or more component solvents, which have different boiling points. There might be one jet fire when one solvent reaches its boiling point. In this way, at least 3 jet fires can be observed for a LIB with ternary solvents. The small organic molecules that burst during the TR process between T_2 and T_3 can also be ignited to form additional jet fire. Therefore, theoretically, there might be 4 jet fires for LIBs with a ternary electrolyte system. However, no more than 3 jet fires are observed in experiments, because the jet fires can combine depending on the characteristic temperatures. Specifically, the boiling points of ordinary carbonates that are used as solvents can be quite similar (DMC 90°C, EMC 108°C, and DEC 128°C), and the vent valve may hold for a while after a boiling point is reached; therefore, the jet fires at approximate 100°C–130°C

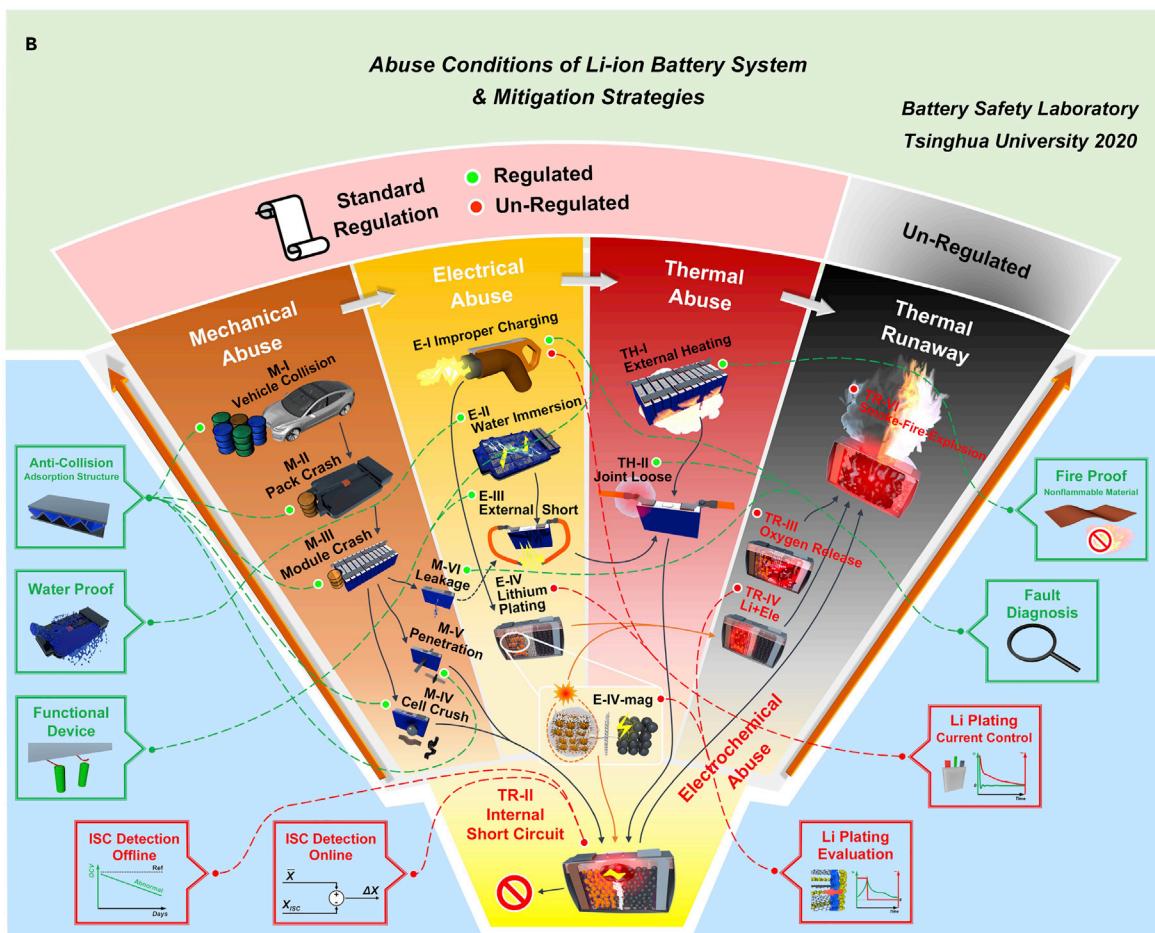
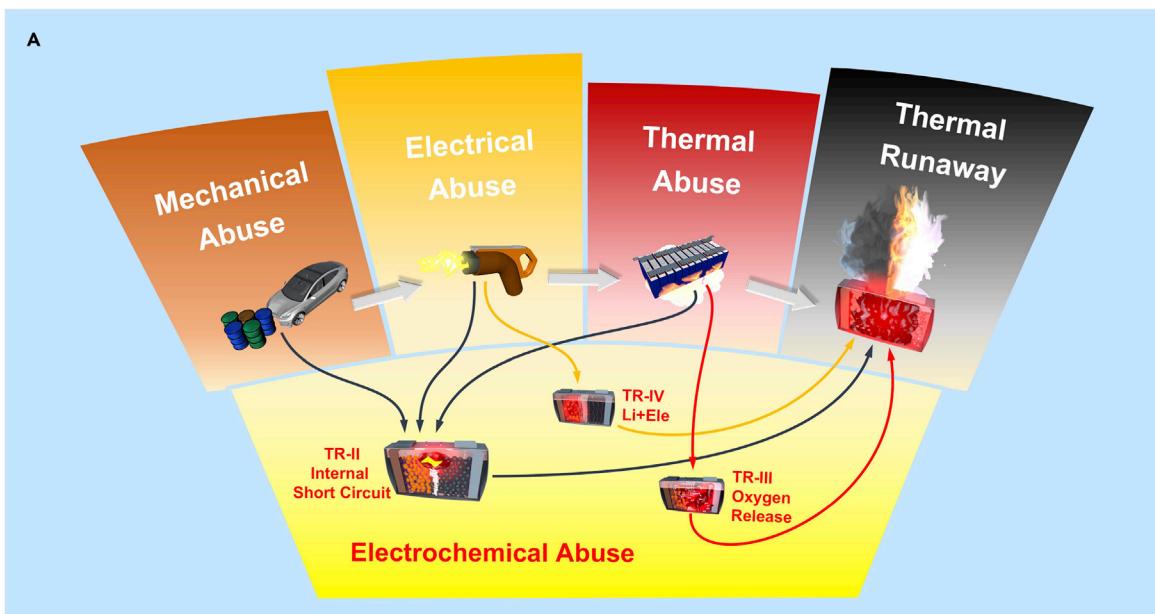


Figure 5. Abuse Conditions of LIB System and Correlated Mitigation Strategies

(A) The relationship between abuse conditions and battery thermal runaway. Besides the mechanical, electrical, and thermal abuse, there might be a new kind of abuse condition named the “electrochemical abuse” that explains the underlying abuse conditions that trigger thermal runaway.

(B) A detailed figure of Figure 5A. From left to right, the abuse conditions can be classified by mechanical abuse, electrical abuse, and thermal abuse. From bottom to top, the abuse conditions are for material, cell, module, pack, and vehicle. Each node (material, cell, module, pack, or vehicle) that locates within the sector represents a unique abuse condition (or we can also call it “state”) that may further trigger thermal runaway. The code on the shoulder of the node denotes the name of the abuse conditions. The prefix M means mechanical abuse, E means electrical abuse, and T means thermal abuse. The arrows between nodes represent the evolution of a failure from initiation to thermal runaway. We may have specific strategies to avoid the occurrence of individual abuse conditions. The specific mitigation strategies that are placed at side have been connected with the correlated abuse conditions through dotted lines, of which the end is marked by a green or red dot. The green dot means that the abuse condition has been considered in some of the test regulations or standards, whereas the red dot means that the abuse condition has not been considered in any of the test regulation or standard yet.

may combine. Moreover, the boiling point of EC (250°C) is close to or higher than an ordinary T_2 ; therefore, the jet fire caused by EC venting will combine with that caused by TR. Regardless of the number of jet fires, the multi-stage jet fires present serious troubles for the fire-fighting of LIBs. The stored fire extinguisher may be largely consumed to wipe out the first jet fire, being insufficient when another jet fire starts. Some reports refer to the multi-stage fire as the troublesome “re-ignition,” but we believe that the underlying mechanisms should be explained by the TSM, as shown in Figure 3B. Although the first jet fire is extinguished in the OUT path, the IN path still evolves and heats the cell to a considerably high temperature, at which point another jet fire would start. In summary, the TSM advises that the fire-extinguishing process of the LIBs must consider not only the fire in the OUT path but also the synergistic inhibition of the chemical reactions in the IN path.

The IN path and OUT path meet (at the top of Figure 3B) when the venting becomes intense during the TR. Black smoke has been observed in several TR cases. The TSM also helps to explain the mechanisms of the color of smoke observed in most experiments. The black smoke, which contains a large amount of the active materials at the cathode, indicates that the inner temperature of the lithium-ion cell exceeds the melting point (660°C) of the aluminum collector. White or gray smoke usually occurs at the earlier state V-II or V-III (in Figure 3B), because the major content of the smoke is the vapor of the electrolyte. The thick particles that rush out during the violent venting at the state V-IV may blow out the fire because they may isolate oxygen from the flammable gases for a while. Re-ignition is possible when the venting stops. Sometimes re-ignition inside a lithium-ion cell is possible because the IN and OUT systems merge; consequently, the hot flammable debris inside the cell can encounter air.

Precise TR mitigation can be achieved once the TR mechanisms depicted by the TSM have been fully understood, as shown in the blue region at the side of Figure 3B. The quantified mitigation target of battery TR is to increase T_1 and T_2 and decrease T_3 and $\max\{dT \cdot dt^{-1}\}$. The prevention strategy can be chemical, mechanical, electrical, or thermal, as long as it can inhibit the triggering process, as shown in Figure 3B. A more stable SEI, which can be obtained using electrolyte additives,¹⁷ is beneficial for increasing T_1 . Considering the TR-trident for increasing T_2 , we should balance the three failure temperatures by coordinated strategies. To postpone the occurrence of state TR-II, a strong separator with a high resistance against the shrinkage at high temperatures, i.e., a separator with ceramic coating¹⁸ and separators coated with boron nitride nanotubes,¹⁹ might be helpful. Another effective method involves increasing the internal resistance of the lithium-ion cell once a short circuit occurs.²⁰ Additionally, we can use thermo-responsive polymer switching materials at the transition temperature to shut down the circuit for internal short.²¹ To cope with the state TR-III, blocking the release pathway by coating^{22,23} is intuitively employed

to mitigate the oxygen release from the cathode; however, occasionally, good coating requires an in-depth study of the validity throughout the life cycle. We want a technique that can immediately capture the active oxygen once it is released from the cathode surface; however, we still do not have a specific solution. Changing the secondary structure from a polycrystalline to a single-crystal morphology might help because it reduces the surface area for oxygen release. To improve the thermal stability of the anode (for manipulating the state TR-IV), electrolyte additives are required to improve the strength of the SEI against thermal stability issues¹⁷ and to improve the uniformity of the SEI to suppress dendrite growth.²⁴ Coating the anode with Al₂O₃ may also be useful for suppressing the dendrite growth, but still with lithium deposition under the coated layer.²⁵ We want to decrease both the maximum temperature (T_3) and the heat release rate ($\max\{dT \cdot dt^{-1}\}$) in the state TR-V and TR-VI. The directive involves neutralizing the oxidant and reductant for relatively mild reactions to occur during the TR. A new concept, which we refer to as the “self-poisoned” technique, might be helpful in reducing the total energy release or diminishing the heat release rate.²⁰ Current literature has some good works on the cell design with the “self-poisoned” function, including (1) the use of thermo-responsive materials to block the contact between the cathode and anode^{26,27} and (2) isolating the damaged area by the structural design of current collectors.²⁸ A coarse setting “self-poisoned” technique was proposed by Liu et al., using an electrospun separator with a core-shell structure containing a flame-retardant liquid within the microfiber.²⁹

We believe that more on the “self-poisoned” technique will appear under the guidance of the TSM in the near future. For the fire-extinguishing process at the OUT path, prevention strategies are suggested to focus on breaking the fire triangle. First, we need to properly design a vent valve that can control the moment of rupture at a proper temperature. Diluting the flammable gases into an extreme lean zone using inertia gases might be helpful.³⁰ The battery cells can be wrapped by inertia gases in their practical applications as well. Flame retardants can be added into the electrolyte³¹ or nonflammable electrolyte.^{32,33} However, occasionally, the flame retardants may have a negative effect on the performances of LIBs. Recent research shows that nonflammable electrolytes with high salt-to-solvent ratios might be good for balancing the safety and performance of LIBs.³⁴ Increasing the thermal stability of electrolyte can also help improve the safety of LIBs. A shift in the venting schedule can be achieved by solvent replacement, and this can significantly help regulate the start time of the fire.

We should note that the sequence of failure events at the cell level might be more complicated than what is being presented in the TSM. There are still many trivial factors that are sensitive to the TR behavior but not included in the TSM. Although equipped with the TSM, we still need well-trained industrial practitioners to properly perform the mitigation strategy and design a good cell. Moreover, the mitigation strategies described above should have a negligible effect on the performances of the LIBs and be cost-effective. This explains why more mitigation strategies are being developed at the system level rather than at the cell level. TR mitigation at the system level is beneficial and critical for the safe utilization of LIBs.

MITIGATING THE THERMAL RUNAWAY PROPAGATION AT THE SYSTEM LEVEL

At the system level, TR occurs in one cell, after which it propagates to adjacent cells, as shown in Figure 4. Figure 4A shows that the TR propagation also occurs via two

pathways for the failure development, similar to the dual paths in [Figure 3](#). An expected failure sequence indicates the TR propagation driven by heat transfer, as shown by the gray arrow in the lower path in [Figure 4A](#). An undesired failure sequence indicates the TR propagation caused by gas and fire propagations, as shown by the red arrow in the upper path in [Figure 4A](#). We call the lower path “expected,” because the blocking of heat transfer is relatively easy. The upper path is called “undesired,” because the propagation of gas and fire has uncertainties, which make it difficult to prevent the failure propagation via this pathway. The failure states may migrate from the lower path to the upper path, once the following conditions are satisfied: (1) gas migration, (2) integrity loss, and (3) fire ignition. To mitigate the TR propagation at the system level, we would prefer to restrict the failure propagation at the lower path.

[Figure 4B](#) illustrates a detailed TSM for the TR propagation at the system level. The expected failure sequence should be the horizontal path, as shown in [Figure 4B](#). First, TR propagates within a battery module, from the triggering cell to its neighbors (state P-TR-II). Second, the TR propagates from the failure module to adjacent modules (state P-TR-III). If the speed of TR propagation can be well controlled, no catastrophic hazard will occur, and we can expect venting to occur through the safety valve. The hazard is acceptable under this case, even with fire. The expected failure sequence may transit to the undesired fire hazard in practical applications. The first transition point (from the expected path to the undesired path) may commence after TR is triggered. The inappropriate design of vent valve and the pack wrap, i.e., where the pressure resistivity of the pack wrap is lower than that of the vent valve, results in unexpected venting, where the gas does not merge from the vent valve. Vented flammable gases may be ignited spontaneously once the fire triangle requirement is satisfied. The second transition point (from the expected path to the undesired path) may commence when TR propagates from module to module. Some observations in the pack test indicate that the cells in the adjacent modules may undergo TR simultaneously, due to the highly intense side heating. The high-intensity heat released at the second transition point increases the possibility of transfer from the expected path to the undesired path, comparing with that case at the first transition point. In other words, controlling the TR at the system level becomes highly difficult when more energy is released during the TR propagation. The slope line (as shown in [Figure 4B](#)) concludes the failure sequence under the undesired fire hazard. Please note that the process in the horizontal path still goes on, although the undesired fire hazard has been initiated. The two paths move forward in parallel directions, accelerating each other using the energy released from the TR propagation. The heat release by fire is larger than that by TR; consequently, the evolving speed of the two paths will be significantly accelerated once the sloping path process starts. If the TR propagation is not well controlled, the two paths will merge at state “P-F-III” (in [Figure 4B](#)), at which point the battery pack deflagrates and finally burns the vehicle (state P-F-IV).

Controlling the speed of TR propagation in the expected failure sequence (the horizontal path in [Figure 4B](#)) is more fundamental in the TR mitigation at the system level. Therefore, we want more countermeasures against the initiation of TR. Anti-abuse designs are presented in [Figure 5](#). The mitigation design usually incorporates the safety design requirements for battery thermal management systems. We need to manipulate the heat-transfer pathway to inhibit the TR propagation between adjacent cells. Effective methods include thermal insulation, reinforced heat dissipation, and fast discharge adjacent cells to lower state of charge.³⁵ Setting thermal barriers between cells and modules is the cost-effective solution mitigating the TR

propagation between cells and modules. Thermal barriers can be made using perlite, glass fiber, ceramic plate, rock wool panel, calcium silicate, silica aerogel,³⁵ graphite composite sheet, Al extrusion,³⁶ phase change materials,³⁷ etc. The thermal barriers must have low thermal conductivity ($<0.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and high working temperature ($>600^\circ\text{C}$) to maintain integrity at TR conditions. The effect of thermal insulation will be enhanced, if the thermal barrier can absorb a large amount of heat. The heat absorption can be achieved using materials with high heat capacity or using phase change materials. We may require composite materials that have comprehensive properties, e.g., some components for maintaining the integrity at high temperatures, and some others for heat insulation or absorption. It is still difficult to cope with the dilemma of heat dissipation (for battery thermal management) and thermal insulation (for TR propagation prevention). However, safety design must consider the influence of the operation mode of the battery thermal management system on the mitigation capability of TR propagation.³⁸ The industry is acquiring solutions that employ accessories in the thermal management system, e.g., side panel, cooling plate, cover board, etc. Occasionally, cooling plates have negative effects on the prevention of TR propagation because their contribution to heat conduction might be larger than their contribution to heat dissipation. Model-based tools are urgently required to solve the nexus of TR propagation prevention,³⁹ as experiments or tests are expensive, and always have low repeatability. Moreover, we wish to note that the design parameters for the prevention strategies that are used in the expected failure sequence should be determined with repeated proof and revision to avoid the catastrophe associated with the undesired sloping path.

The first shift point from the expected path to the undesired path can be cut off by setting a predetermined failure point to control the venting of hot gases.⁴⁰ The target can be achieved by proper design of the vent valve and strengthening of the package to eliminate the weakest point. There is no specific approach to controlling the second transition point; however, the TR should always propagate at mild speed. The prevention of fire hazard at the system level inherits some approaches from that at the cell level (as in Figure 3B). Available countermeasures include using fire-resistant materials to protect the accessories within the battery pack, diluting the flammable gas with inert gas into the extreme lean zone, wrapping the battery cell with inertia gases (e.g., N₂ or Ar₂), using flame retardants to inhibit reactions that are related with fire, introducing an explosive powder that can spread the flame retardants rapidly, and other methods that can extinguish fire outside the cell. Additionally, to protect passengers, fire-resistant layers might be essential to insulate the battery pack from the cabin.

In summary, a cell with a relatively higher energy density can still be used as long as TR can be prevented at the system level. At the system level, the failure propagation is coupled with heat generation and heat transfer under a large temperature gradient. Failure propagates not by simple heat transfer but by heat-reaction-coupled transfer. Mitigation strategies involve cutting off the heat-reaction-coupled transfer among the battery cells. Sometimes we need to combine methods to cope with the intense energy released during TR. For instance, thermal insulation not only blocks the heat transfer but also causes heat accumulation within a limited region. There should be a correlated dredging design to disperse the accumulated heat, similar to a diversion channel employed in auxiliary dams to control flood. Model-based tools are essential for the safety design of battery thermal management systems considering both the prevention of TR propagation and heat dissipation. Intensive efforts should be devoted to restricting the propagation in the horizontal path, as shown in Figure 4B, because some cases in the sloping path with fire might

be uncontrollable. The mitigation strategies based on anti-explosion and fire-extinguishing theories might help handle the undesired fire hazard; however, the unique feature of battery TR needs to be considered. Eliminating or reducing the origin of TR is also important. Anti-abuse strategies will be described in the next section.

AVOIDING THE OCCURRENCE OF THERMAL RUNAWAY

The goal of the safety design of battery systems is to reduce the possibility of abuse, eliminate abuse once it occurs, and create TR alert systems at the earliest stage. An effective mitigation strategy that helps avoid the occurrence of TR is founded on the mechanisms of abuse conditions.

Figure 5 attempts to clarify the nexus of abuse conditions. **Figure 5A** shows that almost all kinds of abuse conditions can be classified into three, including mechanical abuse, electrical abuse, and thermal abuse. It is considerably easy to simulate the three kinds of abuse conditions using test methods (those in standards or regulations). However, in recent years, the test standards keep falling behind due to the emerging new chemistries, e.g., high-nickel-content cathode, anode containing silicon composite, thinner separators, etc., which is challenging. The lag of the test standards can also be caused by the excessive utilization of the LIBs to full capability, e.g., extremely fast charging, extra-low- or extra-high-temperature operation, etc. We should be aware that there is an ever-lasting abuse type underneath the mechanical, electrical, and thermal abuse; this abuse is called the “electrochemical abuse.” The electrochemical abuse occurs when we force the cell to work beyond its capability in electrochemical power outputs. When we develop cells with new chemistries, the safe working window may become narrow, which increases the occurrence possibility of “electrochemical abuse.” In addition, we are forcing the cell to work beyond maximum capacity under specific conditions, making the cell reach its limit of safe operation.

Figure 5B illustrates the details of the abuse conditions that contain various sub-conditions. The abuse states (as shown in **Figure 5B**) may transfer from one to others until TR occurs. A mechanical abuse will develop into an electrical abuse, while an electrical abuse may develop into a thermal abuse, which finally triggers TR. For instance, cell crushing (mechanical abuse) will lead to internal short circuiting (electrical abuse) and the heat (thermal abuse) generated by the internal short circuit triggers TR. If the state transfer is faster than we can identify, the TR will be seemingly triggered by an abuse condition rather than by the thermal abuse. Regardless of the type of abuse condition, T_2 and the TSM are waiting there for the triggering of TR. However, there are still “ghost” failures that trigger TR, but we lack information on them. Some researchers believe that these “ghost” failures might be caused by a “latent effect” that evolves during operation. The “latent effect” throughout the whole cycle life requires more study in the future.

Figure 5B shows that the abuse conditions can occur at the system level, module level, cell level, or material level. The abuse state also transfers from the system level to the material level. For mechanical abuse, a car crash causes deformation of the battery pack, which, consequently, deforms the battery module, within which the cell is crushed. A crushed cell will exhibit internal short-circuiting once the separator (at the material level) fails to isolate the cathode and anode. For electrical abuse, representative causes include improper charging, water immersion, and external short-circuiting as representatives. Improper charging includes overcharging or improper fast charging that may cause lithium plating on the anode. Water

immersion will lead to external short-circuiting, accompanied by the generation of flammable gases.⁴¹ Interestingly, the flammable gases mainly originate from the leaked electrolyte, rather than the hydrogen generated during water electrolysis.⁴¹ For thermal abuse, a known case involved joint loose, which caused overheating. All the other kinds of abuse conditions may finally develop into thermal abuse, which directly heats the battery to extremely high temperatures. The above abuse conditions can easily be characterized at the cell level, where the test standards or regulations have more correlated procedures for a safety check.

The test regulations/standards, which are usually set up by governments or organizations to guarantee the quality of the product before sale, are useful to reduce the possibility of field accidents. We should be aware that formulating proper test standards or regulations is always important, particularly considering that the battery industry strongly prefers high-performance materials, which are the most dangerous, and this is not likely to change in the near future. The question is, how can we formulate proper testing methods that are suitable for guaranteeing safety during applications but are not overly harsh to exclude "high-energy" LIBs? Studies have shown that some abuse methods lead to softer failures than others. For example, the National Aeronautics and Space Administration and the National Renewable Energy Laboratory have shown that internal short circuit testing can be used to induce worst-case failure scenarios.^{42,43} This is quite good and should be adopted in the update of new test standards, although it does not mean that the internal short circuit test can replace the other kinds of abuse tests. As shown in Figure 5B, there are many kinds of abuse conditions that may finally trigger TR, and an internal short circuit is only one of them. It would be unreasonable to believe that a cell that passes a single abuse test (e.g., nail penetration) will surely have good overall safety in applications. To ascertain the safety of a newly developed cell, comprehensive test reports must be provided for all kinds of abuse conditions that are written in the granted test standards.

A good test method must reflect all the comprehensive properties that are important in practical applications.⁴⁴ In our view, to guarantee the overall safety of LIBs, all the abuse conditions that have triggered battery accidents should be included in the testing standards. Although the test procedures cannot simulate the exact triggering conditions in various accidents, they can be set with proper simplification as long as they can reflect the worst case of field failures. Despite the requirement of simulating field failures, a standard test procedure must have good repeatability and reproducibility.⁴⁵ The green dots in Figure 5B denote that the current standard tests already consider these marked kinds of abuse conditions. It is due to these standards that billions of commercial electronics, millions of electric vehicles, and hundreds of electric energy storage stations can operate safely for years.

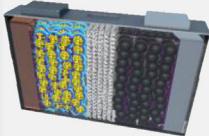
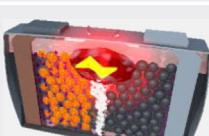
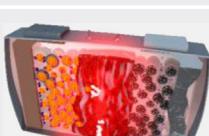
However, new kinds of abuse conditions have emerged secretly at the material level when the industry requires better performances in applications. For instance, the search for low costing raw material has pushed the battery industry to select cathodes with a substantially high nickel content³; however, the thermal stability of a cell with a high-nickel-content cathode reduces significantly when we look at $x \geq 0.8$ in $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$. Another example emerged recently when some entrepreneurs started to provide extreme fast charging for their customers. In our recent results, the T_1 of the cell after extreme fast charging can decrease from 100°C to 60°C (T_2 from 210°C to 100°C).¹² The significant decrease in thermal stability is caused by the lithium plating under the extreme fast charging because the plated lithium is highly reactive with the electrolyte. Moreover, the internal short circuit is another

problem. Spontaneous internal short circuit will appear when we cram more active materials within a cell without suitable separators.⁴⁶ We use green and red dots to distinguish the abuse conditions, ascertaining if they are included in test regulations/standards. Oxygen release, dendrite growth, and internal short circuit (interestingly the arms of the TR-trident in [Figure 3](#), and all at the material level) are the three emerging problems that hide behind macro abuse conditions. These are the initiators of "electrochemical abuse," as mentioned in [Figure 5A](#). Specific countermeasures are in urgent need to cope with the possible hazard caused by the TR-trident. Fortunately, experts in electric vehicle safety-global technical regulation (EVS-GTR), International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC) are working on correlated test procedures to consider the emerging danger. We can trust the battery industry to deliver safe products in the near future, thanks to the ever-evolving standards. The evolving test standards can catch up to the progress in cell chemistries and utilization strategies, as long as the standard formulators are conscious about the "electrochemical abuse" that is underneath the observed abuse conditions. To accurately handle the "electrochemical abuse," one should always have a clear understanding of the safe working window of the components within the LIBs.

Anti-abuse strategies can function at the stage of product design or at the stage of online management. Package design is critical for reducing the severity of the internal short circuit in a car crash situation. The key target of anti-mechanical-abuse strategies is to avoid large deformation that further induces short circuits, as listed in [Table 1](#) for the M-series states. Anti-collision strategies should consider both the crashworthiness and lightweight of the on-board components of electric vehicles.⁴⁷ More rigid structures, energy adsorption structures, and proper displacement of the battery cells are the three useful ways to fortify the battery pack against mechanical abuse. Besides the countermeasures for crush cases (state M-I~M-IV in [Figure 5B](#)), the TR hazard of nail penetration (state M-V in [Figure 5B](#)) can also be mitigated by structures with side-current pathway, first proposed by Samsung SDI.⁴⁸ Leakage (state M-VI in [Figure 5B](#)) is an annoying case that is caused by the rupture of cell packages. Fire or explosion is possible once flammable gases leak from inside the cells, as previously discussed in [Figures 3](#) and [4](#). Volatile organic compound (VOC) sensors might be essential for the fault diagnosis on-board⁴⁹; however, to date, only a few products can meet the requirements for long-term vehicle applications.

The key target of anti-electrical-abuse strategies is to control the electrical energy flow and the electrochemical material flow safely. Charging control is critical for the safe use of LIBs. For overcharging, an active control strategy in the battery management system (BMS) should cut off the circuit once the voltage exceeds the limit, whereas a passive control strategy relies a current interrupting device⁵² that can shut down the charging circuit once gas accumulates inside the cell during overcharge. For extreme fast charging that may cause lithium plating, we need a model-based control algorithm that can adjust the real-time current to guarantee that the anode overpotential is always higher than the threshold potential for lithium plating.⁵³ The model-based control algorithm should be capable of observing the anode overpotential online. The anode overpotential can also be directly measured by the reference electrode, on which we can rely to calibrate the MAP for the fastest charging. The MAP for the fastest charging suggests that there is no fast charging profile without lithium plating. Although the reference electrode still has the problem of longevity, the method for the quick calibration of the charging MAP is spreading in the industry. Heating is also helpful for reducing the problem of lithium plating. Yang et al.⁵¹ accomplished good example of fast charging by proper fast heating,

Table 1. List of Mitigation Strategies that Can Reduce the Thermal Runaway Hazard at Different Levels, Related to Figures 3, 4, and 5

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
3	TR-O	Cell at normal condition		–
	TR-I	Cell heated to a temperature higher than T_1 , indicating the onset of SEI decomposition.		Using electrolyte additives to form more stable SEI. ¹⁷
	TR-II	The separator collapses and the internal short circuit occurs.		(1) Separator with high thermal resistance, e.g., separator with ceramic coating. ¹⁸ (2) Separator coating. ¹⁹ (3) Increase the resistance once short is triggered. ²⁰ (4) Thermo-responsive polymer switching materials. ²¹
	TR-III	The cathode releases active oxygen, which may migrate and oxidize surroundings. ¹¹		(1) Block the release path of oxygen, by coating. ^{22,23} (2) Immediate capturing the active oxygen once it is released. (3) Change the structure to more single crystal to reduce surface area.
	TR-IV	The anode reacts with electrolyte. If there is lithium plating, the plated lithium can react with electrolyte at lower temperature.		Using electrolyte additives to (1) improve the strength against thermal issues. ¹⁷ (2) Improve the uniformity to suppress dendrite growth. ²⁴ Coating the anode with Al_2O_3 to suppress lithium deposition. ²⁵
	TR-V	The cathode and anode mixed together at high temperature. Fast redox reactions release large amount of heat.		Neutralize the oxidant and reductant to have milder reactions. Reduce the total releasing energy or diminish the heat release rate. A new concept called the “self-poisoned” cell. (1) Block the contact between cathode and anode by thermo-response material. ^{26,27} (2) Isolation of damaged area. ²⁸ (3) Core-shell structure containing flame-retardant liquid. ²⁹
TR-VI	TR-VI	Thermal runaway occurs because of fierce redox reactions between the materials inside the cell.		For chemical reactions, there might be no way to stop. For the fire cases, prevention strategies function according to fire triangle.

(Continued on next page)

Table 1. Continued

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
	V-O F-O	Cell at normal condition, no venting or fire. Assume the electrolyte has ternary components: DMC, DEC, and EC. The length of bars indicates the content that remains in the cell.		–
	V-I F-O	The cell swells because of gas generation. (1) The vaporization of the electrolyte component starts at their boiling points, e.g., DMC @90°C and DEC @128°C. The length of the bars denotes the remaining liquid content. (2) The reaction at the anode generates gas.		–
	V-II F-I	The solvent that has boiling point between 90°C and 130°C may gasify and gather abundant gas within the cell. The vent valve opened, with white or gray vapor observed. Fire may occur once the fire triangle is satisfied.		Extinguishing the fire hazard requires breaking the fire triangle: (1) Proper design of vent valve that opens at proper temperature. (2) Dilute the flammable gas with inert gas into extreme lean zone. ³⁰ (3) Wrap the battery cell with inert gases, e.g., N ₂ or Ar ₂ . (4) Using flame retardants to inhibit reactions that are related with fire. ³¹ (5) Using nonflammable electrolyte. ^{32,33} (6) Using high-concentration electrolyte. ³⁴ (7) Using aqueous electrolyte. ⁵⁰ (8) Using solid-state electrolyte. ⁵¹ (9) Other methods that can extinguish fire outside the cell.
	V-III F-II	The solvent EC that has boiling point at approximate 250°C may gasify and push the vent valve open. Fire may occur once the fire triangle is satisfied.		
	V-IV F-III	Large amount of gas exhausts from the cell after thermal runaway, black smoke observed. Fire may occur once the fire triangle is satisfied.		

(Continued on next page)

Table 1. Continued

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
4	P-TR-O	Battery pack at normal condition		–
	P-TR-I	Thermal runaway triggered in one cell under some kind of abuse conditions, as shown in Figure 5		The anti-abuse design can be found in Figure 5 .
	P-TR-II	Thermal runaway propagation between adjacent cells, within a module		Thermal insulation, ³⁵ reinforced heat dissipation, ³⁹ or fast discharge to lower SOC. ³⁵ Thermal barrier between cells and modules. Thermal barrier should have (1) Low thermal conductivity (2) High working temperature
	P-TR-III	Thermal runaway propagation from module to module		–
	P-TR-IV	The exhaust gas might be ignited, but under control		–
	P-V-I	Venting from the side seal		Set a predetermined failure point to mitigate the venting of hot gas ⁴⁰ : (1) Proper design of vent valve (2) Strengthen the package, and diminish the weak points

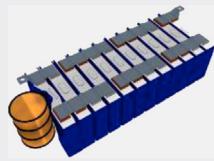
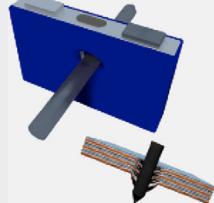
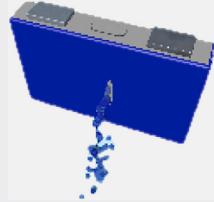
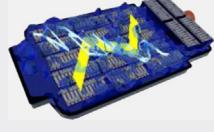
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Table 1. Continued

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
5	P-V-II	Venting from the top cover		
	P-F-I	Fire triggered by the gas vented from side seal		Extinguishing the fire hazard requires breaking the fire triangle: (1) Use fire-resistant material to protect the accessories within the battery pack (2) Dilute the flammable gas with inert gas into extreme lean zone (3) Wrap the battery cell with inert gases, e.g., N ₂ or Ar ₂ (4) Using flame retardants to inhibit reactions that are related with fire (5) Explosive powder that can spread the flame retardants fast (6) Other methods that can extinguish fire outside the cell
	P-F-II	Fire triggered by the gas vented through the cover		
	P-F-III	Pack detonation		
	P-F-IV	Car burning due to battery fire		Use fire-resistant material to insulate the battery pack from the cabin.
5	M-I	Car crash		Countermeasures to collision and crush avoid deformation that may cause short circuit. The anti-collision strategies should consider both crashworthiness and lightweight. ⁴⁷ (1) More rigid structure. (2) Energy adsorption structure. (3) Proper displacement. ⁴⁰
	M-II	Pack deformation		

(Continued on next page)

Table 1. Continued

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
	M-III	Module crush		
	M-IV	Cell crush		
	M-V	Cell penetration		Besides the counter measures for M-I~M-IV, the thermal runaway hazard of nail penetration can also be mitigated by structure with side-current-pathway inside the cell. ⁴⁸
	M-VI	Cell leakage		The leaked carbonate solvent can be detected by gas sensors that can detect volatile organic compound. ⁴⁹
	E-I	Improper charging		For overcharge, active control strategy in BMS will cut off the circuit once the voltage exceeds the limit. Passive control strategy relies on current interrupt device that can cut off the charging circuit. ⁵² For fast charging with possible lithium deposition, see the solutions for E-IV.
	E-II	Water immersion		Water-proof level IP6X (recommended X ≥ 7).
	E-III	External short circuit		Using current interrupt device ⁵² or positive temperature coefficient

(Continued on next page)

Table 1. Continued

Figure No.	State Code	Name and Description	State Photograph	Possible Mitigation Strategy for the State Transition from Previous State ^a
				device to shut down the circuit under overcurrent cases.
	E-IV	Lithium plating		For fast charging, we need model-based control algorithm that can observe the anode overpotential to avoid lithium plating. ⁵³ Despite online current control, MAP for fast charging can be acquired with the help of reference electrode.
	E-IV-mag	Lithium plating magnified, with dendrite growth		We can evaluate the degree of lithium plating by: (1) Offline: NMR, ⁵⁴ neutron diffraction, ⁵⁵ or cryogenic electron microscopy, ⁵⁶ to quantify the amount of plated lithium (2) Online: characteristic voltage plateau. ⁵⁷
	T-I	External heating		Under fire cases, nonflammable material can be used for fireproof design.
	T-II	Local heat point caused by weakened contact		Fault diagnosis methods based on voltage signal that is used to infer contact resistance. ⁵⁸
	TR-II	Internal short circuit		For offline detection, the open-circuit voltage or the self-discharge current ⁵⁹ can be used. For online detection, algorithms can be developed relying on voltage, temperature, or other signals measured by BMS. ⁶⁰

^aPlease note that the more important thing is to know the mechanisms of battery TR. We have not checked the validity of all the listed countermeasures in our lab, and some of them may be still far away from industry application, but we believe that they may shed light on the directions that we can explore in the future. There is a wish, there is a way.

which significantly reduced the possibility of lithium plating. Once lithium plating occurs, there are several approaches that can evaluate the amount of plated lithium. Offline evaluation of plated lithium can rely on nuclear magnetic resonance (NMR)⁵⁴ or neutron diffraction.⁵⁵ Recent progress shows the possibility of using titration gas chromatography and cryogenic electron microscopy to quantify the plated lithium in cells.⁵⁶ Online evaluation of the plated lithium is also possible through a characteristic voltage plateau.⁵⁷ Moreover, an external short circuit should be avoided in applications. Water immersion may cause an external short circuit with a lightning arc that may pierce the cell cases, resulting in leakage of flammable electrolytes.⁴¹ The level of waterproofing is recommended to be IP6X (X ≥ 7). A current interrupting device or device with a positive temperature coefficient is also useful for

terminating the circuit under overcurrent cases, although, occasionally, but sometimes they do not work as expected.⁶²

The internal short circuit occurs in more than 90% of the abuse conditions. Broadly speaking, the internal short circuit occurs when the cathode and the anode encounter each other due to the failure of the battery separator.⁵ The internal short circuit can be caused by (1) mechanical abuse, when the separator is broken by penetration or crush; (2) electrical abuse, when the separator is pierced by dendrite growth; and (3) thermal abuse, when the separator collapses at a high temperature. The BMS should be able to identify the possibility of a short circuit at an early stage, armed with model-based fault diagnosis algorithms. For offline detection, the open-circuit voltage or the self-discharge current⁵⁹ is helpful. For online detection, methods can be built relying on the voltage, temperature, or other signals measured by the BMS.⁶⁰ A fault diagnosis algorithm with combined information of the internal short circuits, flammable gases, and pressure inside the pack will be capable of identifying TR at an early stage.⁶³ New sensors might provide alternatives for the internal short circuit detection, e.g., Wu et al.⁶⁴ demonstrated the usage of a bifunctional separator to provide a new signal that can help identify dendrite growth before it develops into an internal short circuit.

The target of anti-thermal-abuse strategies is to control the temperature of LIBs in a safe operating zone. The temperature control task is usually shouldered by the thermal management system. Nonflammable materials can be utilized for fireproof design, under cases with external combustions. A typical kind of thermal abuse is the overheating caused by the weakened contact of connecting bars. The contact resistance can be monitored by fault diagnosis approaches based on voltage characteristics.⁵⁸ For the control of other cases of thermal abuse, we may return to the situation of TR control shown in Figure 3. Overall, TR mitigation encompasses many issues, and here, a closed loop is formed.

SUMMARY AND OUTLOOK

To the best of our knowledge, we have presented an updated overview of TR mitigation strategies for LIBs. Opportunities exist for researchers and engineers to solve the safety problems associated with high-energy LIBs for their last mile before applications. The mitigation strategies can work at the material level, cell level, and system level, guaranteeing the overall safety of an electric energy storage system that uses LIBs. The mitigation strategies can be chemical, mechanical, electrical, or thermal, as long as they carry out any of the following failure mitigation steps: (1) reduce the possibility of abuse conditions, (2) eliminate the abuse conditions once they occur, (3) enhance the thermal stability of battery cell against abuse conditions, (4) diminish the energy released under a TR case, (5) identify potential TR and warn at the earliest stage, and (6) mitigate the propagation hazard and restrict the damage in a limited area. Based on this, everyone can contribute to enhancing the safety of LIBs with their unique techniques.

We encourage the following research directions that may help the TR mitigation in the future:

Reaction Regulation Guided by the Time Sequence Map

We suggest that a researcher should have a clear understanding of the TSM of the TR mechanism, regardless of the kind of technique he or she is attempting to develop to improve the safety of LIBs. The TSM helps save time in developing solutions because

the trial should be accurate to function at specific reaction routes. A database containing the failure properties of chemical reactions, including the thermodynamics,⁷ kinetics, reactants, and products, needs to be formed to solidify the usage of a TSM. Hopefully, a time will come when the TR mitigation techniques are developed quantitatively under the guidance of the TSM, although additional studies are required to develop such a new theory.

Thermally Stable Components, Such as Cathode, Anode, Electrolyte, etc., to Enhance the Intrinsic Safety of LIBs

Although we have almost exploited all the anode and cathode possibilities, we still have solid electrolytes to count on.⁵¹ Replacing the flammable organic carbonate solvents with intrinsically nonflammable solid-state electrolytes (including polymer, oxide, and sulfide solid-state electrolytes) can be the ultimate solution to the safety issues associated with electrolytes. Besides the solid electrolyte, the development of safe solvents, additives, and lithium salts, such as a fluorinated electrolyte, can help reduce the flammability of the electrolyte. High-concentration electrolyte, or the "solvent-in-salt" electrolyte might also be beneficial for improving the safety performance of lithium-ion cells.⁵⁰ We recommend that further work focuses on the modification of the electrolyte-electrode interface because the surface coating can adequately change the TR behavior.²² For the cathode, surface coating or changing the secondary particle from a polycrystalline morphology to a single-crystal morphology can inhibit the reaction at the cathode-electrolyte surface by reducing the contact area. For the anode, the stability of the SEI layer is very important.⁶⁵ Surface coating²⁵ or artificial formation² are promising strategies for stabilizing the SEI layer, thereby improving the thermal stability. However, we should note that newly developed material should bear comprehensive properties, such as durability, energy and power density, and cost, not just safety.

"Smart Batteries" with Smart Materials and Design

Smart batteries contain components that can operate autonomously under specific cases.⁶⁶ Smart materials for battery safety design rely on mechanisms that can release negative response toward faults. As TR is accompanied by temperature rise, thermal-responsive materials are favored as smart materials for increasing the electric resistance,⁶⁷ blocking the ionic transport,²¹ and releasing a poisoning reagent that can suppress TR²⁹ at specific temperatures. Positive temperature coefficient (PTC) materials are a special kind of thermal-responsive material. PTC materials can be applied by mixing them with the electrode or by coating on the surface of the electrode. Organics with relatively high functional temperatures ($\sim 100^{\circ}\text{C}$) can also function as thermal-responsive materials. Thermal-responsive polymers can be used to block ionic transport under a TR case,⁶⁸ whereas embedded microspheres can melt and cover the electrode to block ion transport.⁶⁹ A poisoning reagent that can neutralize the reactivity between cathode and anode might be helpful in diminishing the heat released during TR, although the poisons must be released under failure conditions rather than normal conditions. Thus, a core-shell structure²⁹ might be essential for the smart release of poisons under a TR case. For the design of poisons, one should consider how the poison functions in relation to the TSM. It is important to know whether the poison suppresses internal short circuit, chemical reactions, or combustion.

The suppression of Li plating is accomplished by self-healing separators.⁶⁶ Silica nanoparticles embedded in separators can react with the penetrating lithium dendrites, thereby retarding the growth of the lithium dendrite.⁷⁰ A sandwich structure is also beneficial for the early detection of an internal short circuit that is induced by

dendrite growth.⁶⁴ Moreover, embedded temperature, voltage, or force sensors are beneficial not only for monitoring the internal states but also for providing immediate information for mitigation operations. For instance, the reference electrode can facilitate the online detection of the anode potential to monitor lithium plating. Fast charging without lithium plating for LIBs can be achieved through online measurement of the anode potential using a reference electrode.⁵³

Safety Monitoring by Intelligent Battery Management System

We recommend the next-generation BMS to have upgraded sensors, models, and data-processing methods. For the upgraded sensor, we recommend sensors or chips that can be embedded inside the cell for immediate fault diagnosis. As was mentioned in the paragraph above, the functional separator and reference electrode are two promising candidates that address this issue. The working direction is to improve the adaptability of the embedded sensor with the electrochemical system inside the cell and to extend the service time of the embedded sensor. For the upgraded model, pioneering researchers are constructing mechanistic models, with many internal states that are observable under the control theory, into next-generation BMSs.⁷¹ Predictably, the future BMS will be more intelligent in monitoring the internal status (including fault information) of LIBs, aided by embedded sensors and reduced-order models.

For the upgraded data-processing methods, artificial intelligence algorithms can process big data to predict possible safety events. Nowadays, massive data are recorded during the daily operation of electric vehicles and uploaded to a cloud monitoring system. Considering the challenge of disposing large amounts of data, data-driven methods using machine learning may help build models to process the data using cloud computing technology.⁷² A successful practice has been demonstrated in Severson et al.,⁷³ which uses machine learning tools to predict the battery cycle life before capacity degradation occurs. In further studies, we encourage the use of data-driven methods that can predict on-board faults based on the recorded data that are uploaded to the cloud. Remote diagnosis, early warning and active mitigation of TR rely on the accurate data-driven prediction on the cloud. This early identification and notification can prevent potential accidents at the earliest stage, significantly reducing the possibility of field failure.

Model-Based Safety Design of Battery Systems

Conventionally, safety tests are expensive and have limited repeatability. Simulation tools are urgently required to reduce the cost of safety tests, particularly for the safety design at the system level. A reliable model can generate a safety envelope virtually, setting a safety boundary for battery systems.⁷⁴ TR models are currently used to guide the safety design of LIBs at both the cell⁹ and system levels.³⁹ The research direction for the TR models include (1) improving the model accuracy and (2) reducing the computational load. The accuracy of the TR model can be improved by establishing amendment dynamics upon chemical reactions, e.g., simulating the venting process and the combustion process. The accurate calibration of the parameters is also essential and requires considerable attention.

Optimally, the safety design should create a balance between the performance and safety, simultaneously. Model-based optimizations are essential for addressing this issue. Any feature that we want to optimize must be simulated simultaneously with the safety issues, by mathematical equations. These kinds of models are called “multi-physic and multi-scale” models,⁷⁵ and the equations that link multi-physics are called “coupling equations.” Several challenges still hinder the utilization of

multi-scale-multi-physic models. First, the quantitative relationship between the safety behaviors at the material and cell levels is still unclear. We still do not know how the electrode modification influences the TR behavior of the lithium-ion cell. Second, the coupling mechanisms of the mechanical, electrical, and thermal abuse conditions still require further study. Third, the question on how to balance the accuracy and computational efficiency remains unanswered.

Heat Dredging in Thermal Management Systems

Effective heat dredging strategies should be considered in the safety design of battery thermal management systems, particularly for preventing the TR propagation. The heat flow should be dredged via reasonable pathways. The challenge is that the energy release is intensive (>10 kW at peak for high-energy cells), forming huge thermal gradient between the triggering point and the neighboring cells. First, heat blocking is essential in delaying the triggering of TR in adjacent cells by fast heat conduction.³⁵ Second, the heat should not be allowed to accumulate within the failure point; therefore, rapid heat dissipation or cooling mechanisms are recommended for lowering the temperature of the TR cell. The thermal barriers must have low thermal conductivity and a high working temperature. However, there is a contradiction between the thermal insulation under the TR condition and heat dissipation under the normal condition. We propose that a smart thermal-responsive material be employed to cope with this dilemma if a high thermal conductivity is observed under normal condition and low thermal conductivity under the TR condition. Phase change materials might benefit the prevention of TR propagation by heat absorption⁷⁶; phase change materials with large latent heat and good thermal conductivity should be further developed. The development of a composite structure that can contain the phase change material and skeletons that can withstand extreme temperature is encouraged to prevent TR propagation. The battery thermal management system can actively respond a TR triggering event, if it can reinforce the cooling coefficient under extreme conditions. Flooding the failure region with a coolant might be a promising strategy, if one does not want an extra fire-extinguishing system on board. We strongly suggest that there should be little fire during the TR propagation process. Since fire makes the situation hopeless, we need to pay more attention to eliminating the possibility of ignition. Generally, to allow sufficient time for rescuing trapped passengers in an accident, the battery thermal management system should be able to delay the TR propagation for at least 40 min (including the time for the brigade to arrive on-site and for the trapped passengers to be evacuated). An obvious trade-off exists between the safety design cost and the delay of TR propagation. Simulation tools are uniquely beneficial for balancing the safety design cost and the prevention of TR propagation.

Proper Test Method to Evaluate Safety Performance

Safety tests should be designed to reproduce abuse conditions experienced by the cell, module, and system in practical situations. Although several testing standards and regulations for LIBs exist, some problems remain unsolved and require further investigation. At the cell level, reliable test methods for simulating the latent-induced internal short circuit requires further study.^{43,45} At the pack level, the global committee of EVS-GTR and ISO are working together to find solutions to prevent the TR propagation on-board.^{77,78}

As the capability of existing cells is increasingly and harshly exploited, we should pay more attention to the “electrochemical abuse” that lies underneath the mechanical, electrical, and thermal abuses. Designing visionary standards that can predict failure cases in the future requires a conscious awareness of the safe working window for all

kinds of LIBs. For the emerging new chemistries, e.g., lithium metal cells, silicon-based cells etc., current test procedures must be adapted to evaluate their overall safety. Furthermore, we should remember that if one wants to ascertain the safety of a newly developed cell system, he or she must provide comprehensive test reports for all kinds of abuses, as a single abuse test may not reflect the worst-case scenarios for the newly developed sample.

Moreover, we encourage researchers to establish reasonable test methods for evaluating the safety of lithium-ion cells. Unsolved problems include the following: (1) identification of TR, not by naked eye observation but with measurement signals, (2) repeatability of the TR triggering process, (3) elucidating the rationale behind for penetration and overcharge tests, (4) equivalency of the TR result by different triggering methods, and (5) evaluation of the safety of aged cells, etc.

Finally, in [Summary and Outlook](#), we remind researchers to pay attention to the safety performance when developing new chemistries. High energy density, fast charging and discharging, and excellent longevity are the top priorities in developing new cell chemistries; however, the safety problem hides behind the “priority three” and hinders the utilization of “better” materials. Hopefully, our efforts can help mitigate the TR of LIBs more easily, increase the safety and availability of former unsafe cells, and suppress failure propagation under extreme conditions. We expect that researchers would collaborate to guarantee the overall safety of LIB systems in the near future.

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AUTHOR CONTRIBUTIONS

X.F. wrote the paper. D.R. contributed contents in the [Summary and Outlook](#). X.F., D.R., and X.H. reviewed and revised the paper. M.O. and X.H. proposed the concept and the structure of this perspective.

REFERENCES

1. Hur, J.I., Smith, L.C., and Dunn, B. (2018). High areal energy density 3D lithium-ion microbatteries. Joule 2, 1187–1201.
2. Tu, Z., Choudhury, S., Zachman, M.J., Wei, S., Zhang, K., Kourkoutis, L.F., and Archer, L.A. (2017). Designing artificial solid-electrolyte interphases for single-ion and high-efficiency transport in batteries. Joule 1, 394–406.
3. Olivetti, E.A., Ceder, G., Gaustad, G.G., and Fu, X. (2017). Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals. Joule 1, 229–243.
4. Wang, Q., Mao, B., Stolarov, S.I., and Sun, J. (2019). A review of lithium ion battery failure mechanisms and fire prevention strategies. Prog. Energy Combust. Sci. 73, 95–131.
5. Feng, X., Ouyang, M., Liu, X., Lu, L., Xia, Y., and He, X. (2018). Thermal runaway mechanism of lithium ion battery for electric vehicles: a review. Energy Storage Mater. 10, 246–267.
6. Feng, X., Fang, M., He, X., Ouyang, M., Lu, L., Wang, H., and Zhang, M. (2014). Thermal runaway features of large format prismatic lithium ion battery using extended volume accelerating rate calorimetry. J. Power Sources 255, 294–301.
7. Feng, X., Zheng, S., Ren, D., He, X., Wang, L., Cui, H., Liu, X., Jin, C., Zhang, F., Xu, C., et al. (2019). Investigating the thermal runaway mechanisms of lithium-ion batteries based on thermal analysis database. Appl. Energy 246, 53–64.
8. Feng, X., Sun, J., Ouyang, M., He, X., Lu, L., Han, X., Fang, M., and Peng, H. (2014). Characterization of large format lithium ion battery exposed to extremely high temperature. J. Power Sources 272, 457–467.
9. Feng, X., He, X., Ouyang, M., Wang, L., Lu, L., Ren, D., and Santhanagopalan, S. (2018). A coupled electrochemical-thermal failure model for predicting the thermal runaway behavior of lithium-ion batteries. J. Electrochem. Soc. 165, A3748–A3765.
10. Feng, X., Zheng, S., He, X., Wang, L., Wang, Y., Ren, D., and Ouyang, M. (2018). Time sequence map for interpreting the thermal runaway mechanism of lithium-ion batteries with $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathode. Front. Energy Res. 6, 126.
11. Liu, X., Ren, D., Hsu, H., Feng, X., Xu, G.L., Zhuang, M., Gao, H., Lu, L., Han, X., Chu, Z., et al. (2018). Thermal runaway of lithium-ion batteries without internal short circuit. Joule 2, 2047–2064.
12. Li, Y., Feng, X., Ren, D., Ouyang, M., Lu, L., and Han, X. (2019). Thermal runaway triggered by

- plated lithium on the anode after fast charging. *ACS Appl. Mater. Interfaces* 11, 46839–46850.
13. Feng, X., Ren, D., Zhang, S., He, X., Wang, L., and Ouyang, M. (2019). Influence of aging paths on the thermal runaway features of lithium-ion batteries in accelerating rate calorimetry tests. *Int. J. Electrochem. Sci.* 14, 44–58.
14. Noh, H.J., Youn, S., Yoon, C.S., and Sun, Y.K. (2013). Comparison of the structural and electrochemical properties of layered Li $[Ni_xCo_yMn_z]O_2$ ($x=1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85) cathode material for lithium-ion batteries. *J. Power Sources* 233, 121–130.
15. Larsson, F., Bertilsson, S., Furlani, M., Albinsson, I., and Mellander, B.E. (2018). Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-LiCoO₂ cells at different levels of ageing. *J. Power Sources* 373, 220–231.
16. Wang, Q., Huang, P., Ping, P., Du, Y., Li, K., and Sun, J. (2017). Combustion behavior of lithium iron phosphate battery induced by external heat radiation. *J. Loss Prevent Proc.* 49, 961–969.
17. Ma, L., Xia, J., Xia, X., and Dahn, J.R. (2014). The impact of vinylene carbonate, fluoroethylene carbonate and vinyl ethylene carbonate electrolyte additives on electrode/electrolyte reactivity studied using accelerating rate calorimetry. *J. Electrochem. Soc.* 161, A1495–A1498.
18. Zhang, Z. (2002). Separator for a high energy rechargeable lithium battery. US Patent 6432586 B1, Filed, April 10, 2000, and granted, August 13, 2002. <https://patentimages.storage.googleapis.com/8d/ac/6f/3d6339a0f4bed1/US6432586.pdf>.
19. Rahman, M.M., Mateti, S., Cai, Q., Sultana, I., Fan, Y., Wang, X., Hou, C., and Chen, Y. (2019). High temperature and high rate lithium-ion batteries with boron nitride nanotubes coated polypropylene separators. *Energy Storage Mater.* 19, 352–359.
20. Noelle, D.J., Shi, Y., Wang, M., Le, A.V., and Qiao, Y. (2018). Aggressive electrolyte poisons and multifunctional fluids comprised of diols and diamines for emergency shutdown of lithium-ion batteries. *J. Power Sources* 384, 93–97.
21. Chen, Z., Hsu, P.C., Lopez, J., Li, Y., To, J.W.F., Liu, N., Wang, C., Andrews, S.C., Liu, J., Cui, Y., et al. (2016). Fast and reversible thermoresponsive polymer switching materials for safer batteries. *Nat. Energy* 1, 15009.
22. Xu, G., Liu, Q., Lau, K.K.S., Liu, Y., Liu, X., Gao, H., Zhou, X., Zhuang, M., Ren, Y., Li, J., et al. (2019). Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes. *Nat. Energy* 4, 484–494.
23. Hou, P., Zhang, H., Deng, X., Xu, X., and Zhang, L. (2017). Stabilizing the electrode/electrolyte interface of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ through tailoring aluminum distribution in microspheres as long-life, high-rate, and safe cathode for lithium-ion batteries. *ACS Appl. Mater. Interfaces* 9, 29643–29653.
24. Liu, K., Liu, Y., Lin, D., Pei, A., and Cui, Y. (2018). Materials for lithium-ion battery safety. *Sci. Adv.* 4, eaas9820.
25. Friesen, A., Hildebrand, S., Horsthemke, F., Börner, M., Klöpsch, R., Niehoff, P., Schappacher, F.M., and Winter, M. (2017). Al₂O₃ coating on anode surface in lithium ion batteries: impact on low temperature cycling and safety behavior. *J. Power Sources* 363, 70–77.
26. Ji, W., Jiang, B., Ai, F., Yang, H., and Ai, X. (2015). Temperature-responsive microspheres-coated separator for thermal shutdown protection of lithium ion batteries. *RSC Adv* 5, 172–176.
27. Shi, Y., Noelle, D.J., Wang, M., Le, A.V., Yoon, H., Zhang, M., Meng, Y.S., Fan, J., Wu, D., and Qiao, Y. (2017). Mitigating thermal runaway of lithium-ion battery through electrolyte displacement. *Appl. Phys. Lett.* 110, 063902.
28. Naguib, M., Allu, S., Simunovic, S., Li, J., Wang, H., and Dudney, N.J. (2018). Limiting internal short-circuit damage by electrode partition for impact-tolerant Li-ion batteries. *Joule* 2, 155–167.
29. Liu, K., Liu, W., Qiu, Y., Kong, B., Sun, Y., Chen, Z., Zhuo, D., Lin, D., and Cui, Y. (2017). Electrospun core-shell microfiber separator with thermal-triggered flame-retardant properties for lithium-ion batteries. *Sci. Adv.* 3, e1601978.
30. Li, W., Wang, H., Zhang, Y., and Ouyang, M. (2019). Flammability characteristics of the battery vent gas: a case of NCA and LFP lithium-ion batteries during external heating abuse. *J. Energy Storage* 24, 100775.
31. Kalhoff, J., Eshetu, G.G., Bresser, D., and Passerini, S. (2015). Safer electrolytes for lithium-ion batteries: state of the art and perspectives. *ChemSusChem* 8, 2154–2175.
32. Chawla, N., Bharti, N., and Singh, S. (2019). Recent advances in non-flammable electrolytes for safer lithium-ion batteries. *Batteries* 5, 19.
33. Chen, S., Zheng, J., Yu, L., Ren, X., Engelhard, M.H., Niu, C., Lee, H., Xu, W., Xiao, J., Liu, J., et al. (2018). High-efficiency lithium metal batteries with fire-retardant electrolytes. *Joule* 2, 1548–1558.
34. Zeng, Z., Murugesan, V., Han, K.S., Jiang, X., Cao, Y., Xiao, L., Ai, X., Yang, H., Zhang, J., Sushko, M.L., and Liu, J. (2018). Non-flammable electrolytes with high salt-to-solvent ratios for Li-ion and Li-metal batteries. *Nat. Energy* 3, 674–681.
35. Feng, X., He, X., Ouyang, M., Lu, L., Wu, P., Kulp, C., and Prasser, S. (2015). Thermal runaway propagation model for designing a safer battery pack with 25 Ah LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ large format lithium ion battery. *Appl. Energy* 154, 74–91.
36. Yuan, C., Wang, Q., Wang, Y., and Zhao, Y. (2019). Inhibition effect of different interstitial materials on thermal runaway propagation in the cylindrical lithium-ion battery module. *Appl. Therm. Eng.* 153, 39–50.
37. Kshetrimayum, K.S., Yoon, Y.G., Gye, H.R., and Lee, C.J. (2019). Preventing heat propagation and thermal runaway in electric vehicle battery modules using integrated PCM and micro-channel plate cooling system. *Appl. Therm. Eng.* 159, 113797.
38. Li, Q., Yang, C., Santhanagopalan, S., Smith, K., Lamb, J., Steele, L.A., and Torres-Castro, L. (2019). Numerical investigation of thermal runaway mitigation through a passive thermal management system. *J. Power Sources* 429, 80–88.
39. Feng, X., Lu, L., Ouyang, M., Li, J., and He, X. (2016). A 3D thermal runaway propagation model for a large format lithium ion battery module. *Energy* 115, 194–208.
40. Arora, S., Shen, W., and Kapoor, A. (2016). Review of mechanical design and strategic placement technique of a robust battery pack package for electric vehicles. *Renew. Sustain. Energ. Rev.* 60, 1319–1331.
41. Xu, C., Ouyang, M., Lu, L., Liu, X., Wang, S., and Feng, X. (2017). Preliminary study on the mechanism of lithium ion battery pack under water immersion. *ECS Trans.* 77, 209–216.
42. Walker, W.Q., Darst, J.J., Finegan, D.P., Bayles, G.A., Johnson, K.L., Darcy, E.C., and Rickman, S.L. (2019). Decoupling of heat generated from ejected and non-ejected contents of 18650-format lithium-ion cells using statistical methods. *J. Power Sources* 415, 207–218.
43. Finegan, D.P., Darst, J., Walker, W., Li, Q., Yang, C., Jervis, R., Heenan, T.M.M., Hack, J., Thomas, J.C., Rack, A., et al. (2019). Modelling and experiments to identify high-risk failure scenarios for testing the safety of lithium-ion cells. *J. Power Sources* 417, 29–41.
44. Chen, S., Niu, C., Lee, H., Li, Q., Yu, L., Xu, W., Zhang, J.-G., Dufek, E.J., Whittingham, M.S., Meng, S., et al. (2019). Critical parameters for evaluating coin cells and pouch cells of rechargeable Li-metal batteries. *Joule* 3, 1094–1105.
45. Liu, L., Feng, X., Zhang, M., Lu, L., Han, X., He, X., and Ouyang, M. (2020). Comparative study on substitute triggering approaches for internal short circuit in lithium-ion batteries. *Appl. Energy* 259, 114143.
46. Feng, X., Ouyang, M., and Lu, L. (2018). Overview about accidents: selected lessons learned from prior safety-related failures of Li-ion batteries. In *Electrochemical Power Sources: Fundamentals, Systems, and Applications: Li-Battery Safety* (Elsevier), pp. 571–606.
47. Li, Z., Duan, L.B., Cheng, A.G., Yao, Z.P., Chen, T., and Yao, W. (2018). Lightweight and crashworthiness design of an electric vehicle using a six-sigma robust design optimization method. *Eng. Optim.* 51, 1393–1411.
48. Moon, J., and Ahn, B. (2013). Secondary Battery Having Insulation Bag. US Patent 9196886/B2. Filed, Aug. 30, 2010, and granted, Nov. 24, 2015. <https://patentimages.storage.googleapis.com/6c/0a/a4/6bc31b8955636c/US9196886.pdf>.
49. Pan, Y., Feng, X., Lu, L., and Ouyang, M. (2019). Early warning of thermal runaway for lithium-ion battery based on multi-sensor detection. The Electrochemical Society. <https://iopscience.iop.org/article/10.1149/MA2019-016/590>.

50. Yang, C., Chen, J., Qing, T., Fan, X., Sun, W., von Cresce, A., Ding, M.S., Borodin, O., Vatamanu, J., Schroeder, M.A., et al. (2017). 4.0 V aqueous Li-ion batteries. Joule 1, 122–132.
51. Kato, Y., Hori, S., Saito, T., Suzuki, K., Hirayama, M., Mitsui, A., Yonemura, M., Iba, H., and Kanno, R. (2016). High-power all-solid-state batteries using sulfide superionic conductors. Nat. Energy 1, 16030.
52. Byun, S.W., Yoo, S.Y., Lee, C.Y., and Lee, K.H. (2016). Rechargeable Battery Having Short-circuit Protrusion. U.S Patent 14/732,484. Filed, Jun 5, 2015, and granted, Feb. 11, 2016. <https://patentimages.storage.googleapis.com/8f/a6/fc/e9755a489e1a36/US20160043379A1.pdf>.
53. Chu, Z., Feng, X., Lu, L., Li, J., Han, X., and Ouyang, M. (2017). Non-destructive fast charging algorithm of lithium-ion batteries based on the control-oriented electrochemical model. Appl. Energy 204, 1240–1250.
54. Guérin, K., Ménétrier, M., Février-Bouvier, A., Flandrois, S., Simon, B., and Biensan, P. (2000). A ⁷Li NMR study of a hard carbon for lithium-ion rechargeable batteries. Solid State Ionics 127, 187–198.
55. Zinth, V., von Lüders, C., Hofmann, M., Hattendorff, J., Buchberger, I., Erhard, S., Rebelo-Kornmeier, J., Jossen, A., and Gilles, R. (2014). Lithium plating in lithium-ion batteries at sub-ambient temperatures investigated by *in situ* neutron diffraction. J. Power Sources 271, 152–159.
56. Fang, C., Li, J., Zhang, M., Zhang, Y., Yang, F., Lee, J.Z., Lee, M.H., Alvarado, J., Schroeder, M.A., Yang, Y., et al. (2019). Quantifying inactive lithium in lithium metal batteries. Nature 572, 511–515.
57. Petzl, M., and Danzer, M.A. (2014). Nondestructive detection, characterization, and quantification of lithium plating in commercial lithium-ion batteries. J. Power Sources 254, 80–87.
58. Ma, M., Wang, Y., Duan, Q., Wu, T., Sun, J., and Wang, Q. (2018). Fault detection of the connection of lithium-ion power batteries in series for electric vehicles based on statistical analysis. Energy 164, 745–756.
59. Sazhin, S.V., Dufek, E.J., and Gering, K.L. (2017). Enhancing Li-ion battery safety by early detection of nascent internal shorts. J. Electrochem. Soc. 164, A6281–A6287.
60. Feng, X., Pan, Y., He, X., Wang, L., and Ouyang, M. (2018). Detecting the internal short circuit in large-format lithium-ion battery using model-based fault-diagnosis algorithm. J. Energy Storage 18, 26–39.
61. Yang, X.G., Liu, T., Gao, Y., Ge, S., Leng, Y., Wang, D., and Wang, C.-Y. (2019). Asymmetric temperature modulation for extreme fast charging of lithium-ion batteries. Joule 3, 3002–3019.
62. Jeevarajan, J.A. (2011). Hazards associated with high voltage high capacity lithium-ion batteries. ECS Trans. 33, 1–6.
63. Koch, S., Birke, K., and Kuhn, R. (2018). Fast thermal runaway detection for lithium-ion cells in large scale traction batteries. Batteries 4, 16.
64. Wu, H., Zhuo, D., Kong, D., and Cui, Y. (2014). Improving battery safety by early detection of internal shorting with a bifunctional separator. Nat. Commun. 5, 5193.
65. Heiskanen, S.K., Kim, J., and Lucht, B.L. (2019). Generation and evolution of the solid electrolyte interphase of lithium-ion batteries. Joule 3, 2322–2333.
66. Wen, L., Liang, J., Chen, J., Chu, Z.Y., Cheng, H.M., and Li, F. (2019). Smart materials and design toward safe and durable lithium ion batteries. Small Methods 3, 1900323.
67. Zhang, H., Pang, J., Ai, X., Cao, Y., Yang, H., and Lu, S. (2016). Poly(3-butylthiophene)-based positive-temperature-coefficient electrodes for safer lithium-ion batteries. Electrochim. Acta 187, 173–178.
68. Yang, H., Leow, W.R., and Chen, X. (2018). Thermal-responsive polymers for enhancing safety of electrochemical storage devices. Adv. Mater. 30, e1704347.
69. Baginska, M., Blaiszik, B.J., Merriman, R.J., Sottos, N.R., Moore, J.S., and White, S.R. (2012). Autonomic shutdown of lithium-ion batteries using thermoresponsive microspheres. Adv. Energy Mater. 2, 583–590.
70. Liu, K., Zhuo, D., Lee, H.W., Liu, W., Lin, D., Lu, Y., and Cui, Y. (2017). Extending the life of lithium-based rechargeable batteries by reaction of lithium dendrites with a novel silica nanoparticle sandwiched separator. Adv. Mater. 29, 27874235.
71. Chu, Z., Jobman, R., Rodríguez, A., Plett, G.L., Trimboli, M.S., Feng, X., and Ouyang, M. (2020). A control-oriented electrochemical model for lithium-ion battery. part II: parameter identification based on reference electrode. J. Energy Storage 27, 101101.
72. Li, S., Li, J., He, H., and Wang, H. (2019). Lithium-ion battery modeling based on big data. Energy Proced. 159, 168–173.
73. Severson, K.A., Attia, P.M., Jin, N., Perkins, N., Jiang, B., Yang, Z., Chen, M.H., Aykol, M., Herring, P.K., Fragedakis, D., et al. (2019). Data-driven prediction of battery cycle life before capacity degradation. Nat. Energy 4, 383–391.
74. Li, W., Zhu, J., Xia, Y., Gorji, M.B., and Wierzbicki, T. (2019). Data-driven safety envelope of lithium-ion batteries for electric vehicles. Joule 3, 2703–2715.
75. Zhang, C., Santhanagopalan, S., Sprague, M.A., and Pesaran, A.A. (2015). Coupled mechanical-electrical-thermal modeling for short-circuit prediction in a lithium-ion cell under mechanical abuse. J. Power Sources 290, 102–113.
76. Wilke, S., Schweitzer, B., Khateeb, S., and Al-Hallaj, S. (2017). Preventing thermal runaway propagation in lithium ion battery packs using a phase change composite material: an experimental study. J. Power Sources 340, 51–59.
77. Börger, A., Mertens, J., and Wenzl, H. (2019). Thermal runaway and thermal runaway propagation in batteries: what do we talk about? J. Energy Storage 24, 100649.
78. Feng, X., Jin, C., Wang, F., He, X., and Ouyang, M. (2019). Evaluating the thermal runaway propagation within a battery pack: the unsolved problems that hinders the consensus on the test profile in Electric-Vehicle-Safety Global-Technical-Regulation. The Electrochemical Society. <https://iopscience.iop.org/article/10.1149/MA2019-01/6/588>.