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Review

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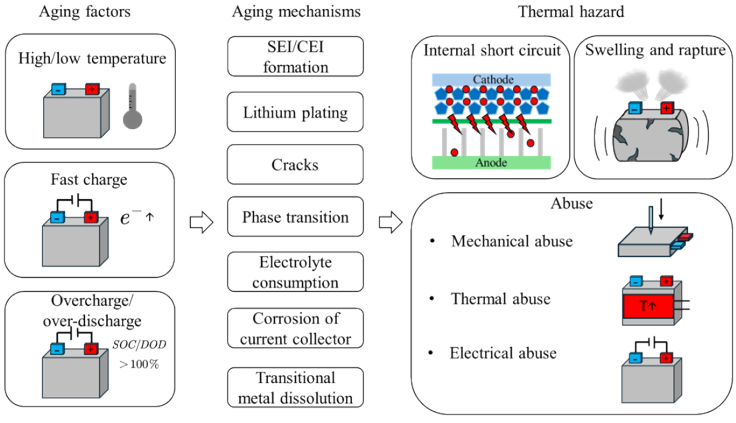
Shuguo Sun and Jun Xu ✉

Graphical Abstract



This review delves into the fundamental aging mechanisms of lithium-ion batteries, highlighting factors that accelerate degradation and their effects on safety behaviors, such as swelling and off-gassing. It systematically examines how aging influences thermal hazards, including internal short circuits and thermal runaway under abusive conditions thus to provide critical insights for designing safer batteries and enhancing predictive safety diagnostics for aged lithium-ion batteries.

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Safety behaviors and degradation mechanisms of aged batteries: A review

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ABSTRACT

As lithium-ion batteries (LIBs) become increasingly widespread, ensuring their safety has become a primary concern. Particularly, battery aging has been reported to significantly impact major battery safety behaviors, including the internal short circuit (ISC) and thermal runaway (TR). Over the past decade, despite considerable research into the thermal hazards of aged batteries, the complexity of battery aging and TR mechanisms, along with the challenges posed by extreme experimental conditions, necessitates a systematic understanding. Aiming to provide a comprehensive review of safety issues related to aged batteries, this paper begins by exploring the fundamental aging mechanisms and factors that accelerate aging. It then investigates how aging affects battery safety issues, including swelling and off-gassing behaviors. Furthermore, we discuss the impact of aging on TR problems induced by abusive conditions, covering safety issues from internal sources to external abusive scenarios. This review offers valuable insights into understanding and predicting the thermal hazards of aged LIBs, which provides guidelines for designing and manufacturing safer LIBs and accurate and rapid battery safety prognostics in the future.

KEYWORDS

battery safety, battery aging, internal short circuit, thermal runaway, modeling, characterization

1 Introduction

To satisfy the growing demands for energy and environmental sustainability, as well as supporting the rapid advancement of modern mobility, lithium-ion batteries (LIBs) have emerged as one of the most essential technologies. LIBs have been widely used in electric vehicles, renewable energy storage systems, and consumer products such as laptops and cell phones. 2,600 GWh LIBs were predicted to be produced in 2030[1]. Based on the current industry design standard, LIBs usually can be charged-discharged for at least 1,000 cycles[2], about 8–10 years of working time. Obviously, with the ever-expanding manufacturing scale of LIBs, it is expected that there will be a huge number of aged cells in various systems. On the other hand, considering the limited resources and high cost for Li and the potential environmental issues[3], LIB recycling and repurposing have become important research topics. In this case, battery aging becomes a key consideration, particularly when aged cells are deployed on a large scale.

Considering the grand challenges in LIB recycling[4], battery repurposing has become another popular and feasible alternative. Battery aging is characterized by the degradation of battery performance due to the complicated internal electrochemical side reactions during battery usage or storage. The state of health (SOH) is a key metric used to quantify battery aging status, defined as the ratio between the capacity of an aged battery and a fresh battery. SOH effectively represents the degree of battery capacity degradation, with lower SOH values indicating more severe aging[5]:

$$\mathrm{SOH} = \frac{C_t}{C_0} \times 100\%$$

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where C_t is the battery capacity at time t and C_0 denotes initial battery capacity.

It is widely accepted that electric vehicle (EV) power batteries reach their end of life when the SOH decreases to 80%[6]. Battery aging leads to irreversible impacts on battery behaviors in many aspects, including capacity degradation and increased internal resistance[7]. Severe degradation can even cause internal short circuits (ISC), posing significant safety hazards[8]. These safety hazards not only exist during the 20% degradation of the SOH but become more dominant, frequent, and severe if the battery SOH drops below 80%[9] for any battery re-purpose scenarios. In recent years, LIB safety issues such as fires and explosions have become a major concern for users/consumers[10,11].

In order to provide a comprehensive overview of the state-of-the-art understanding of the safety of aged batteries, this review will mainly cover battery aging mechanisms, their impacts, and associated safety behaviors. Section 2 introduces the mechanisms of battery aging and the factors influencing it. Aging mechanisms are categorized and described as either *calendar aging* or *cycling aging*, based on the specific scenarios. This section also details the various degradation reactions and their impacts, alongside the major factors that accelerate degradation. Section 3 delves into the safety issues from battery aging, focusing on the risks associated with aging-induced safety problems. It discusses how battery degradation accelerates and can directly lead to the occurrence of ISC or swelling, which may further develop into thermal runaway (TR). Section 4 explores the safety behaviors of aged batteries under abuse scenarios. It identifies the thermal hazards of aged batteries under various abusive conditions, such as thermal, mechanical, and electrical abuse. Additionally, it discusses how aging paths influence battery thermal runaway behavior. Moreover, this study emphasizes the thermal runaway propagation and the modeling of thermal runaway behavior in aged batteries to offer valuable insights for industrial applications and predictive models. Finally, Section 5 summarizes aging mechanisms and the thermal hazards of aged LIBs. It provides insights into the safety of aged batteries and suggests potential directions for future research. This review aims to offer fundamental knowledge and conclusive guidance to researchers and engineers working with LIBs, enabling them to better understand the thermal safety of aged batteries and thereby promote the future development of LIB safety.

2 Aging mechanism

Battery aging refers to the phenomenon of battery capacity loss and increased internal resistance during use[12,13], which adversely affects battery performance and reduces its lifespan[14,15]. Pioneering studies have demonstrated that the battery is a complicated electrochemical system[16] involving multiple side reactions (i.e., solid–electrolyte interphase [SEI] formation, lithium plating, and transitional metal dissolution) during degradation. Battery aging primarily occurs on the anode, cathode, and electrolyte. Electrolyte degradation primarily occurs at the interface between the anode and cathode, where it reacts with electrode active materials and decomposes[17]. Therefore, aging mechanisms will be discussed based on reaction locations (i.e., the anode and cathode) without addressing electrolyte degradation separately.

A few studies employed the scanning electron microscope (SEM) to analyze aged battery electrodes and suggested that the anode undergoes significant morphologic changes after aging, e.g., SEI formation and graphite particle cracking[18,19]. In addition, microcracks can be observed on the cathode side, resulting from the surface reactivity at the cathode-electrolyte interface[20].

Generally, the major aging side reactions can be attributed to the combined effects of loss of lithium inventory (LLI) and loss of active materials (LAM), occurring at both the anode and cathode of the battery[12,21]. LLI refers to the reduction of cyclable lithium ions caused by aging reactions, e.g., surface film formation, decomposition reactions, and lithium plating[22]. LAM involves the reduction of active mass available for lithium-ion insertion due to particle cracking, structural disordering, and loss of electrical contact[22]. Both LAM and LLI contribute to the capacity degradation of batteries, representing various aging processes (e.g., SEI formation and transitional metal dissolution).

2.1 Anode

Aging reactions at the anode significantly influence battery aging. Currently, commercial LIBs predominantly use graphite as the anode, which occupies the largest share of the market. Consequently, the aging mechanisms of these batteries have attracted tremendous attention. Aging reactions at the anode (Fig. 1) include: (1) SEI formation, growth, and decomposition[12,22,27]; (2) electrolyte decomposition[23,28]; (3) structural change of electrode particle (i.e., cracks)[29]; and (4) lithium plating[30].

During battery storage, anode materials react with the electrolyte, leading to its decomposition and causing LLI[31]. The reactions generate a thin passivation layer at the interface of the electrode and electrolyte, known as the SEI. The composition of SEI can differ due to the variations in battery materials and experimental conditions. The following reactions list the most common SEI components (e.g., CH_3OCO_2Li, Li_2CO_3, LiF and ROLi)[32,33].

$$2DMC + 2e^- + 2Li^+ \rightarrow 2CH_3OCO_2Li + C_2H_6 \uparrow \quad (1)$$

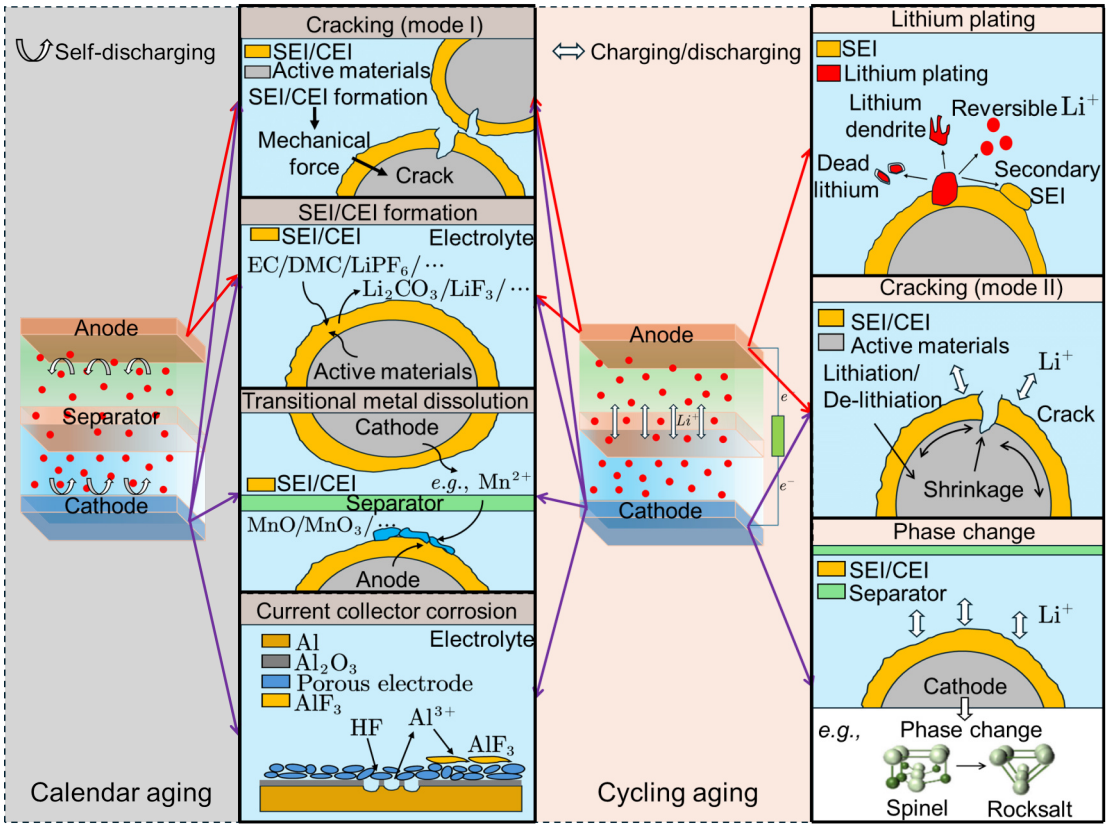

Figure 1 Summary of calendar and cycling major aging mechanism schematics[23–26]. CEI, cathode–electrolyte interphase; DMC, dimethyl carbonate; EC, ethylene carbonate; SEI, solid–electrolyte interphase.

$$EC + 2Li^+ + 2e^- \rightarrow Li_2CO_3 + C_2H_4 \uparrow \quad (2)$$

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \quad (3)$$

$$DOL + e^- + Li^+ \rightarrow C_2H_4O + CH_2OLi \quad (4)$$

where DMC is dimethyl carbonate, EC is ethylene carbonate, and DOL is 1,3-dioxolane.

A stable SEI is essential to prevent further reactions between the anode and electrolyte[34]. SEI formation is considered a major aging reaction on anode. As SEI thickness increases, it creates resistance to lithium-ion flow, resulting in increased battery impedance[35]. Conversely, SEI becomes unstable at high temperatures, accelerating its decomposition and generating low-ion-conductivity lithium salts, thereby increasing battery impedance.

Battery chemistry also governs the performance of SEI by generating different SEI chemistries. SEI components are typically inorganic salt degradation products and organic partial or complete reduction products of electrolyte solvents[36]. Suitable battery materials are crucial for improving SEI performance and extending battery lifetime. Notably, while most LIB systems generate SEI, batteries using lithium titanate oxide as the anode materials do not, since the potential of this materials is within the stable range of the electrolyte[16].

The formation of SEI can induce mechanical force between graphite particles, leading to cracks in the particle (crack mode I)[37]. Active materials exposed to electrolytes due to cracks generate new SEI layers and reduce reversible lithium inventory.

Mechanical stress developed by the intercalation or de-intercalation of Li^+ and gas escape are the main reasons for the structural change of electrode particles (crack mode II). As the battery degrades, the structure of the anode becomes less ordered, reducing the battery capacity — a process known as LAM.

Additionally, transition metal ions (e.g., Mn^{2+}) from the cathode can be transported to the anode by potential difference, reacting with SEI components (e.g., Li_2CO_3, LiF)[38], which conversely promotes the generation of new SEI and consumption of active lithium ion.

$$Li_2CO_3 + [Mn(EC)_6]_2^+ + 2EC = 2[Li(EC)_4]^+ + MnCO_3 \quad (5)$$

$$Li_2CO_3 + [Mn(EC)_6]_2^+ + 2EC = 2[Li(EC)_4]^+ + MnO \quad (6)$$

$$2LiF + [Mn(EC)_6]_2^+ + 2EC = 2[Li(EC)_4]^+ + MnF_2 \quad (7)$$

Besides, Li^+ can be reduced to Li metal and attached to the anode during the battery charging process, i.e., Li plating[39,40]. Li plating is uncommon under normal charging scenarios, but during low-

temperature cycling, fast charging, or overcharging, lithium-ion diffusivity in the electrolyte exceeds that in the anode. As the anode potential is close to the Li plating potential, Li^+ is preferentially reduced to lithium metal on the graphite surface (Eq. (8)).

$$(1-X)Li^+ + (1-X)e^- \rightarrow (1-X)Li \quad (8)$$

In this case, lithium metal aggregation can be observed at the anode–electrolyte interface[41,42]. The major problems caused by lithium plating (Fig. 1) include: (1) polarization due to aggregation of Li^+ at the surface of the anode, hindering charge and discharge performance; (2) lithium metal can react with electrolyte, generating SEI on the electrode surface, insulating part of the lithium metal from the electrolyte, leading to LLI[43]; (3) lithium metal accumulation generating lithium dendrites, potentially blocking or piercing the separator, causing ISC; and (4) lithium metal is redox to lithium ion and return to electrolyte system as reversible lithium[44]. Li plating is an LLI reaction, that promotes SEI growth and electrolyte decomposition. Therefore, it is critical to avoid or reduce Li plating reactions during LIB usage.

Although not a major degradation reaction, copper corrosion has been observed on the anode during over-discharge conditions. Copper is chosen as the current collector for the anode due to its stability under LIBs operation windows. Generally, the anode of a lithium battery is operated under 0~1.5 V potential, below the oxidation potential of copper, preventing the dissolution of copper. However, the anode potential can reach 4 V during overcharging, allowing copper dissolution[45]. During this process, Cu^{2+} ion would be reduced to Cu metal and redeposited on the surface of the anode, resulting in dendrite growth[46].

2.2 Cathode

The major reactions on the cathode can be summarized as: (1) cathode–electrolyte interphase (CEI) formation and growth; (2) transitional metal dissolution; (3) electrode materials structural change (i.e., cracks, phase transition)[47,48]; and (4) Corrosion of electrode[49] (Fig. 1).

Similar to the anode, side reactions occur between cathode materials and the electrolyte due to high potential, generating a protective passive solid electrolyte interphase, also referred to as the CEI in some studies[27]. Common CEI components are composed of LiF, Li_2CO_3, $LiPO_xF_y$, and $LiPF_x$, etc.[50]. Compared to the SEI at the anode, CEI generation is relatively less, making it harder to observe[8]. High temperature promote CEI growth in both cycling and calendar aging tests[51].

For metal oxide cathodes, transition metal dissolution is the main problem that occurs (i.e., LAM)[52]. Transition metal dissolution is often accompanied by electrolyte decomposition, SEI growth, and the transport of dissolved products[8]. CEI formation and transitional metal dissolution are regarded as the main degradation mechanisms of the cathode[53].

Additionally, some researchers suggest that increased battery internal pressure due to thicker SEI during aging leads to cathode surface cracking, resulting in LAM. Besides, a state of charge (SOC)-dependent phase transition is another source for the particle secondary cracks. The Ni-rich layer oxide cathode suffers from multiple degradation due to high electrode reactivity, i.e., CEI formation, gas generation, and phase transition, leading to the most capacity degradation and material structural damage[54,55].

There are three types of LIB material corrosion, i.e., aluminum, lithium, and stainless steel[23]. Aluminum, commonly used as a cathode current collector in LIBs due to its low cost and good electrical conductivity, corrodes due to reaction with the decomposition products of $LiPF_6$ — hydrogen fluoride (HF). Corrosion generates a passivation layer composed of AlF_3 on the electrode surface, leading to an increase in impedance (Eq. (9)).

$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \quad (9)$$

HF also causes the decomposition of cathode metal oxides, generating side reaction products that attach to the surfaces of the anode, separator, and cathode, increasing impedance[45]. Lithium corrosion generally occurs at the anode of lithium metal batteries, involving the reaction between lithium metal and copper current collectors. Stainless steel corrosion involves reactions between the electrolyte and the battery casing[49].

2.3 Aging classification by application

Based on their application modes, LIB aging can be categorized into calendar aging and cycling aging. Battery aging is closely related to how the battery is used. Therefore, this section will discuss the mechanisms of battery aging in the contexts of calendar aging and cycling aging.

2.3.1 Calendar aging

Calendar aging refers to the aging that occurs during the storage of a battery. This type of aging happens continuously and is independent of whether current flows through the battery[15,16]. Battery capacity degrades during storage due to self-discharge, although some of this degradation is reversible[56]. The major factors contributing to battery self-discharge are internal electron leakage (i.e., electronic conductivity of electrolyte), external electron leakage (i.e., external conductors), electrode/electrolyte reactions, partial dissolution of the active

materials, electrode passivation, and mechanical decomposition[57]. Calendar aging is particularly sensitive to environmental temperature and SOC. Both high temperature and high SOC can accelerate the aging process of LIBs.

Major calendar aging reactions on the anode (Fig. 1) are (1) SEI growth, and (2) structural change (i.e., cracks) of the anode particle. The SEI gradually grows during storage, continuously consuming reusable lithium ions, leading to LLI[19]. Specifically, a lower potential at the anode accelerates SEI growth during storage, which is the leading cause of battery capacity degradation during storage[28,58]. Since the current does not affect storage aging, crack mode I is the major reason for the crack generation. Microcracks can be observed on the anode particles during the calendar aging process even under a 0% SOC statement[48].

Calendar aging mechanisms at the cathode (Fig. 1) include: (1) CEI growth; (2) transitional metal dissolution; (3) structural change (i.e., cracks); and (4) battery material corrosion. CEI growth has been discussed in the previous section, increasing with storage time and high storage temperature. Specifically, transitional metal concentration on the anode significantly arises when batteries are stored at high SOC and temperature, subsequently promoting SEI formation on the anode[59]. However, it has been proven that the influence of transition-metal dissolution plays only a minor role in battery calendar aging. Keil et al. investigated the calendar aging at different SOC (0–100%). Transitional metal dissolution is only observed in a few cases with SOC ≥ 90% with little influence on the capacity fading[28]. Besides, battery self-discharge can occur when the cathode potential lies outside the electrolyte electrochemical window, transferring Li^+ from the electrolyte into the cathode. Note that for layered oxide cathodes (e.g., $LiNi_{1-x-y}Mn_xCo_yO_2$ [NCM]), hydrogen transfer to a delithiated cathode results in self-discharge[60]. Self-discharge damages the cathode crystalline structure and causes aluminum current collector corrosion[47].

2.3.2 *Cycling aging*

Cycling aging refers to the degradation of capacity and increase in impedance observed in batteries due to charge and discharge cycles. During this process, extra energy is induced into the electrochemical system, leading to new aging mechanisms. Cycling aging reactions primarily occur at the anode and cathode. A critical difference between cycling aging and calendar aging is that, besides temperature and SOC, the charge-discharge configuration (e.g., current intensity) also influences battery cycling aging.

During the battery cycling, reactions that occur at the anode can be concluded as: (1) SEI growth; (2) structural change (i.e., cracks); and (3) lithium plating (Fig. 1).

Similar to calendar aging, there is SEI formation growth and decomposition during charge and discharge. Specifically, the initial formation of SEI results in approximately a 10% reduction in lithium-ion inventory, occurring during the first charging process. Compared with calendar aging, structural change on the anode is more severe under cycling aging[56]. The volume changes due to Li^+ intercalation or de-intercalation can reach 10% and 300%[61] for graphite and silicon anodes, respectively, along with cracks developing on particle surfaces. These cracks usually appear near the separator due to local high current intensity[62]. Additionally, graphite exfoliation and cracking can happen due to gas escape (e.g., CO, H_2, CH_2), as the result of reduction reactions between the anode and electrolyte when the anode potential exceeds the electrochemical stability window of the electrolyte[63]. In this situation, the contact area between the particles decreases, thus increasing the impedance[8].

As mentioned in Section 2.1, lithium plating is one of the major side reactions that lead to degradation on the anode surface during cycling processes, which does not happen in calendar aging. Significant lithium deposition can be observed when the battery is cycled by high current and low temperature[64].

Major cycling aging mechanisms on the cathode include: (1) CEI formation and growth[65]; (2) transitional metal dissolution[52]; (3) electrode material structural change (i.e., cracks, phase transition)[25]; and (4) corrosion of electrode[45] (Fig. 1).

CEI thickness can increase with cycling numbers, which changes the ionic resistance, affecting cycling performance[66]. Transitional metal dissolution that happen in cycling aging have been discussed in Section 2.2 as major aging reactions on cathodes[67–69].

Different from calendar aging, the cathode structural change is mainly caused by volume change (crack mode I) and phase transition (crack mode II). There is a 10% volume change of the cathode during the battery cycling[14], potentially cracking cathode particles. Furthermore, when the battery cycles under high SOC and temperature, this process cracks cathode metal oxide, leading to loss of contact between particles, which reduces the diffusivity of ions in the electrode[70]. LAM caused by cathode phase transitions and cracking is the primary reason for cathode aging[71]. Li^+ intercalation or de-intercalation may cause irreversible phase transition of cathode materials during cycling[25], especially under high current rate conditions. This damages the lattice structures of the cathode and generates excessive mechanical stress[67]. For $LiMn_2O_4$ (LMO) materials, the irreversible phase transition from cubic to tetragonal is

reported due to volumetric strain and Jahn–Teller distortion during cycling, which leads to the major degradation of cathode materials[64]. The de-lithiation/lithiation process of NCM cathode induces severe crystalline size changes, thus leading to phase transition, especially under high current[72]. $LiFePO_4$ (LFP) cathode generates impurity phases during cycling, promoting the dissolution of transitional metal (i.e., Fe^{2+}, Fe^{3+})[73].

Similar to calendar aging, the corrosion of cathode mainly occurs on the Al current collector, which reduces the contact area between electrode materials and the current collector, thus increasing impedance.

2.4 Influencing factors of battery degradation

Battery degradation corresponds to multiple factors, among which temperature, SOC, and cycling configuration are the major factors influencing this process.

2.4.1 *Temperature*

Temperature has a significant impact on battery aging for both calendar and cycling aging[74]. High and low temperatures contribute to battery degradation through different mechanisms. For most commercial LIBs, the optimal operation temperature is 15~35°C due to potential side reactions and degradation under high or low temperatures[75]. There is a strong correlation between battery temperature (determined by both external ambient temperature and internal side reactions) and battery degradation rate[76]. SEI can be unstable and decomposed under high temperatures, which exposes the anode materials to electrolytes, leading to new SEI formation. High-temperature cycling changes the SEI component proportion with decreasing LiF and increasing $ROCO_2Li$, promoting the generation of irreversible Li_xC_6 so that increases the aging rate[77]. High temperatures accelerate the corrosion of electrode materials (Fig. 2b), thus increasing the battery aging process[79,80].

Acceleration of CEI growth can also be observed at cathode under high environmental temperature, although not significant compared with anode[18]. Wu et al.[81] investigated the degradation of NCM LIBs under 45°C, 65°C and 75°C, proposing that the main reason for battery aging is caused by LLI and an apparent acceleration of battery degradation would be observed when the battery is stored at a temperature above 75°C. The high-temperature performance of LIB is also significantly limited by the electrolyte solvent, such as dimethoxymethane, inducing unstable SEI/CEI at elevated temperature[82].

Besides, electrolyte degradation also occurs due to low thermal stability of $LiPF_6$, leading to decomposition at high temperatures[83].

$$LiPF_6 \rightarrow LiF + PF_5 \quad (10)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (11)$$

On the other hand, low environmental temperature would suppress charge transfer kinetics and diffusion of ions, thus inducing Li plating on the anode (Fig. 2a)[43,84]. There is a change in the battery internal mechanical properties due to low temperature, which would also cause degradation of the battery. Previous studies have shown that storing LIBs at −27°C may deform lattice structure and crack electrode particles, resulting in the degradation of the battery[85].

2.4.2 *State of Charge*

SOC also has an important impact on battery aging[74]. Some studies consider the influence of voltage when discussing battery aging, which corresponds to SOC; therefore, voltage and SOC are considered the same influencing factors in this paper. Storage SOC is one of the most important factors in calendar aging. Keil et al.[28] studied calendar aging of three different types of batteries (NCM, $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ [NCA], and LFP) and suggested that when the battery is stored with high SOC, SEI formation is accelerated due to a relatively

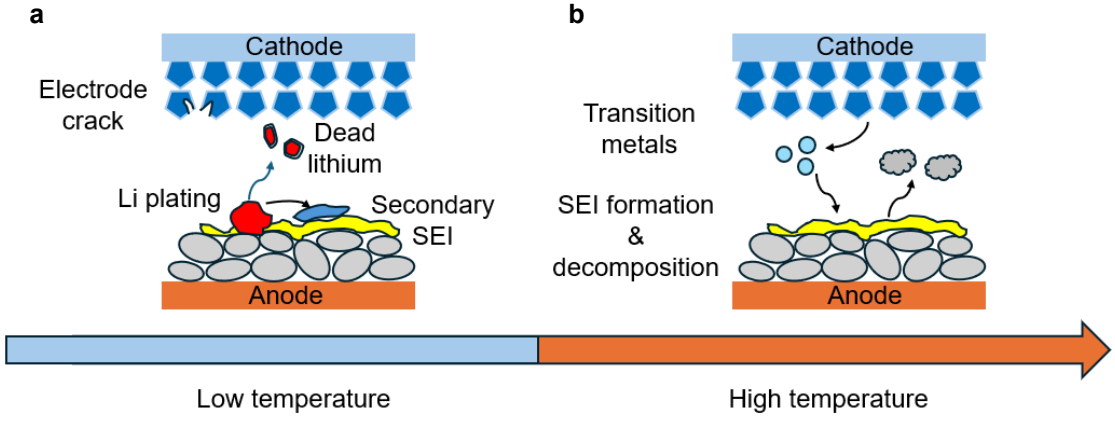

Figure 2 Aging acceleration mechanism of low and high temperature[17,18,78]. SEI, solid–electrolyte interphase.

low potential of the anode, thus increasing LLI. Conversely, when the SOC of the battery is low, corrosion of the negative current collector is promoted by the high potential of the anode, leading to a loss of contact between the electrode and the current collector. Kassem et al.[58] experimentally studied the calendar degradation of LFP/graphite batteries with three different SOCs (30%, 60%, and 100%) and three different temperatures (30°C, 45°C, 60°C). The study demonstrated that both temperature and SOC are significant factors in battery aging, with temperature being a more significant factor than SOC.

On the other hand, SOC influence on cycling aging is represented by depth of discharge (DOD), overcharging, and overdischarging. DOD refers to the SOC range during charging–discharging cycling[86]. DOD is similar to SOC influence but mainly applies to cycling aging. High DOD means batteries are discharged to a lower SOC when the discharge process ends. The battery aging rate is proportional to the DOD[87]. Hoog et al.[79]. investigated the aging rate under different SOC ranges. When batteries are cycling within a high SOC range (60%–100%), SEI and CEI formation reactions are active, leading to a faster aging rate. In contrast, under lower SOC (10%–30%), battery aging is not as evident.

Overcharging and overdischarging during cycling can also accelerate the aging rate, although in most cases, these effects are limited by the battery management system. Overcharge refers to the process where the charge cut-off voltage during cycling is higher than the up-limit voltage of LIBs and it accelerates capacity fading, predominantly due to LLI[88–90]. The main aging mechanism during slight overcharging can be described as side reactions (i.e., Li plating, SEI formation, and transition metal dissolution) due to high potential on the anode and over-lithiation/de-lithiation on the electrode (Fig. 3a). The slight overcharge degradation behavior from 100% SOC to 120% SOC was studied, and it was found that when batteries are within 100%–105% SOC, there is only slight capacity loss and LLI occurs. After the battery is charged to 110% SOC, LAM occurs in the battery (e.g., cathode structure change, transitional metal dissolution)[89,90]. Lithium plating reactions caused by the overlithiation of the anode on the surface of the anode are also observed. After 120% SOC, the battery is no longer slightly overcharging, ISC may be triggered due to deformation and heat accumulation, leading to a voltage drop.

In contrast, over-discharge refers to discharging batteries to a lower cut-off voltage. Different from overcharging, at the initial stage of over-discharge, slight SEI decomposition appears on the anode surface (Fig. 3b). As over-discharge deepens, more severe SEI decomposition happens, exposing the anode to the electrolyte, which leads to new SEI formation in the following recharging process. Over-discharge promotes the dissolution of the copper current collector due to the low potential on the anode, leading to metallic Cu deposition on the surface of the anode. This deposition can hinder lithium ion intercalation, which is the major reason

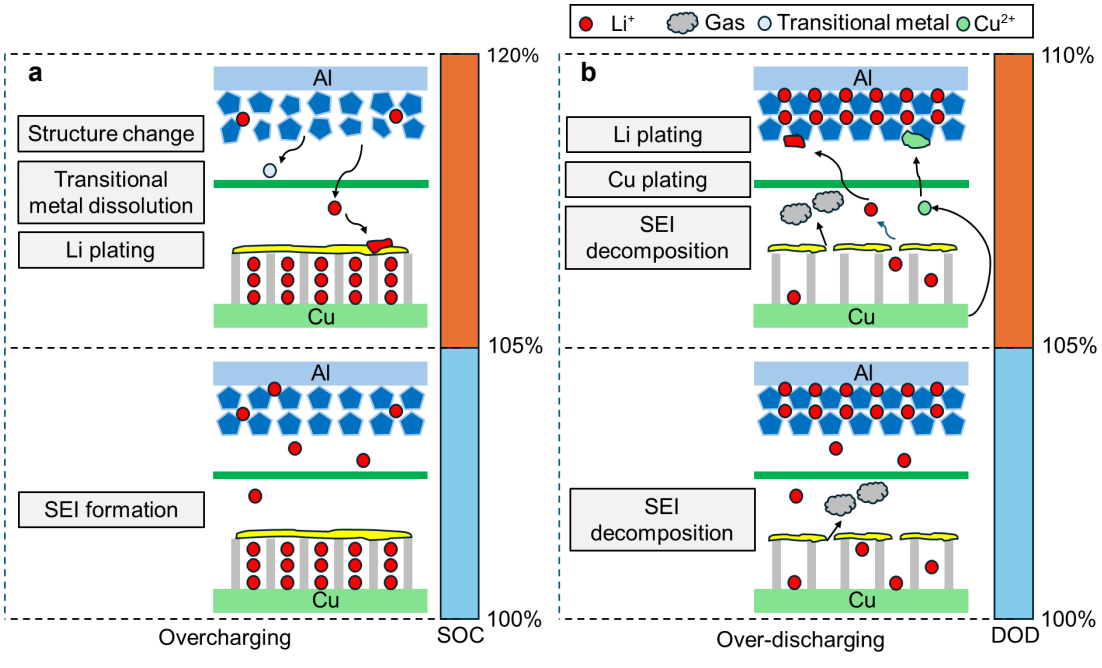

Figure 3 Lithium-ion battery $Li_{0.92}(Ni_{0.84}Mn_{0.05}Co_{0.11})O_2$/Graphite side reactions during overcharging. (a) SOC = 100%–110%; (b) SOC = 110%–120% and during over-discharging; (c) DOD = 100%–105%; and (d) DOD = 105%–110%[90–93]. DOD, depth of discharge; SEI, solid–electrolyte interphase; SOC, state of charge.

for the capacity degradation[94,95]. Lithium plating on the cathode surface is also discovered due to the full intercalation of Li ions[93].

2.4.3 *Charging/discharging rate*

Electrical conditions used in battery cycling are collectively described as cycling configuration, which includes charging/discharging rate. Battery aging is proportional to charging/discharging rate during cycling, with high current rates accelerating Li plating reactions[96]. Charging rate has a higher influence on aging compared to discharging because the charging process leads to severe side reactions on the anode, i.e., lithium plating[97]. The battery aging rate is proportional to charging rate because high charging rate promotes lithium plating reactions[98–102]. For example, "mossy" shaped lithium deposition can be found on the surface of the anode at 80% SOH after fast charging (Fig. 4a). The lithium plating reactions consume electrolytes, leading to LLI and capacity reduction. The mossy lithium deposition and decomposition products of lithium and electrolyte cause pole closure of the separator, increasing the internal resistance. Raj et al.[102] investigated the charging rate dependency of LIBs aging rate. The batteries are cycling under different charging rates varying from 1C to 9C. The results (Figs. 4b and 4c) show that both capacity fading rate and impendence rate increase as the charging rate increases, indicating a higher aging rate under higher charging rate.

Note that the fast-charging experiments are always accompanied by an increase in the battery's internal temperature due to joule heating, especially at extremely high charging rates. Battery maximum temperature can exceed 75°C under 6C fast-charge conditions[103]. As previously mentioned, temperature is also an accelerating factor of aging. As such, there is still room for improvement in experimental design to better isolate and identify the pure impact of charging rate[104].

3 Safety issues arising from battery aging

3.1 Internal short circuit

3.1.1 *Definition of internal short circuit*

Internal short circuit (ISC) refers to the condition where the anode and cathode come into direct

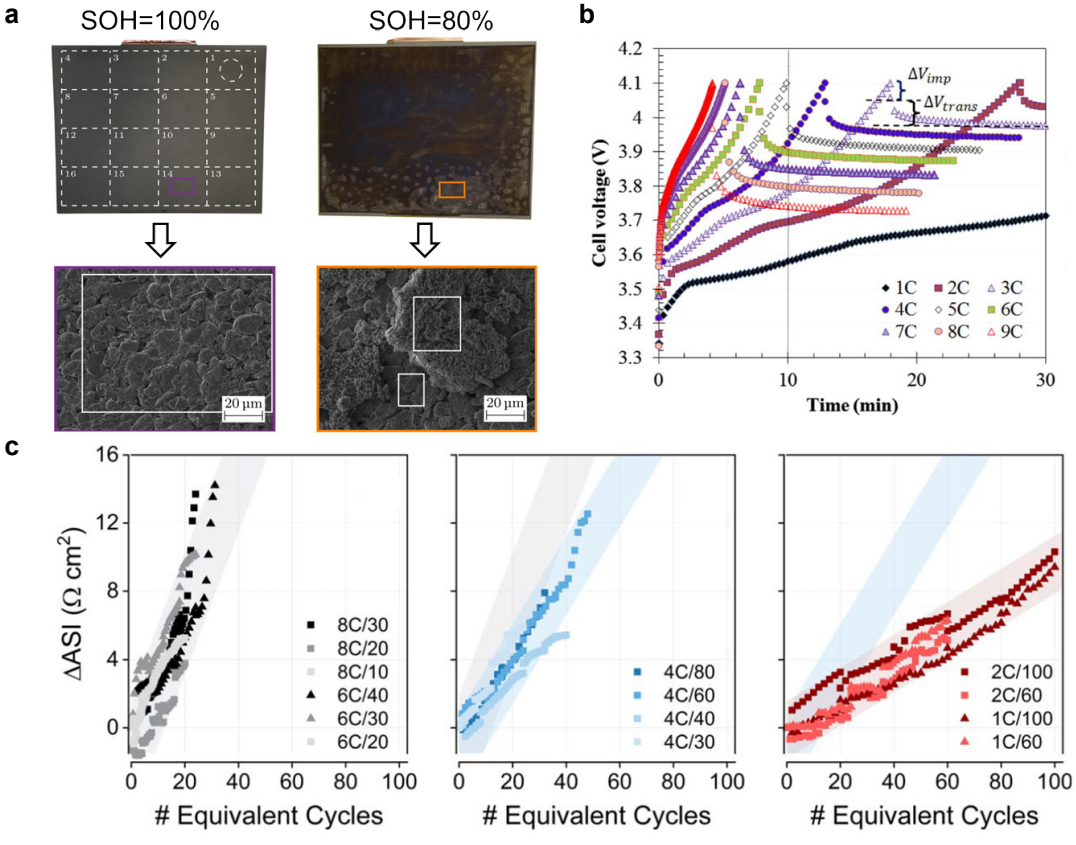

Figure 4 (a) Photographs and SEM micrographs of anode sheets with lithium plating on the surface of anode at 80% SOH. Adapted with permission from Ref. [101] ©2021, Elsevier Ltd. (b) Voltage as a function of time during rate capability test. Reproduced with permission from Ref. [100] ©2019, The Electrochemical Society. (c) Impedance rise as a function of equivalent full cycles for cells tested at 8C, 6C, 4C, 2C, and 1C. Reproduced under the CC BY 4.0 license from Ref. [102] ©2020, The Author(s). ASI, area-specific impedance; SOH, state of health.

contact with each other[105]. The ISC could be defined as four modes depending on the short circuit components: short circuit between anode and cathode (An–Ca), short circuit between anode and aluminum current collector (An–Al), short circuit between the cathode and copper current collector (Ca–Cu), and short circuit between the two current collectors (Al–Cu)[106–109] (Fig. 5a). Generally, ISC can be triggered by mechanical, thermal, or electrical abuse, causing the separator and current collector to melt and subsequently altering the ISC resistance at specific locations[110]. Therefore, ISC resistance is important in influencing thermal runaway behavior. Li et al.[109] designed a set of experiments to quantitatively study and distinguish the resistance of four types of ISC (Fig. 5b). After ISC happens, the Joule heat generated by the short circuit current causes local overheating and finally triggers thermal runaway, leading to fire and explosion[113].

3.1.2 *Battery aging induced internal short circuit*

Since the battery can be simplified as a sandwich structure of anode–separator–cathode, the failure of the separator is the ultimate direct cause of ISC[110,113]. Although the separator does not contribute to the electrochemical performance of the battery, it plays a critical role in battery safety by physically separating the anode and cathode components and ensuring the transportation of ions[114]. As we mentioned in Section 2, the separator is not the main location for aging, however, some aging mechanisms still influence the separator performance in terms of mechanical properties, thermal stability, ionic transportation, and wettability[115,116].

During the aging cycling, degradation products from the electrolyte and anode were found at the separator surface near the anode side. These products reduce the porosity and ionic conductivity, thus leading to an increase in the internal resistance of the separator. Despite this, it has been reported that the separator maintains constant chemical components (i.e., polyethylene, polypropylene) and thermal stability during cycling[115]. However, degradation of the mechanical properties of the separator has been observed. Makki et al.[111] observed some fractures on the anode side surface of the separator upon 4C fast charging cycling (Fig. 5c). This decrease in mechanical strength may lead to early failure of the separator due to internal deformation and external mechanical forces, ultimately causing ISC. Furthermore, battery aging may induce local stress and temperature rise due to Joule heat on the separator, resulting in shrinkage or collapse.

In addition to the degradation, side reactions such as lithium plating may also induce ISC by penetrating the separator. Aging cycling under abusive conditions such as overcharging[117–119], fast charging[44,120], and low temperature charging[121,122] can enhance the occurrence of Li plating. Metallic lithium accumulates on the anode and anode-side separator during cycling to form lithium dendrite[123–125]. Lithium dendrite can penetrate the separator, connecting the cathode and anode directly and triggering the ISC[126]. In the meantime, a few studies also reported that

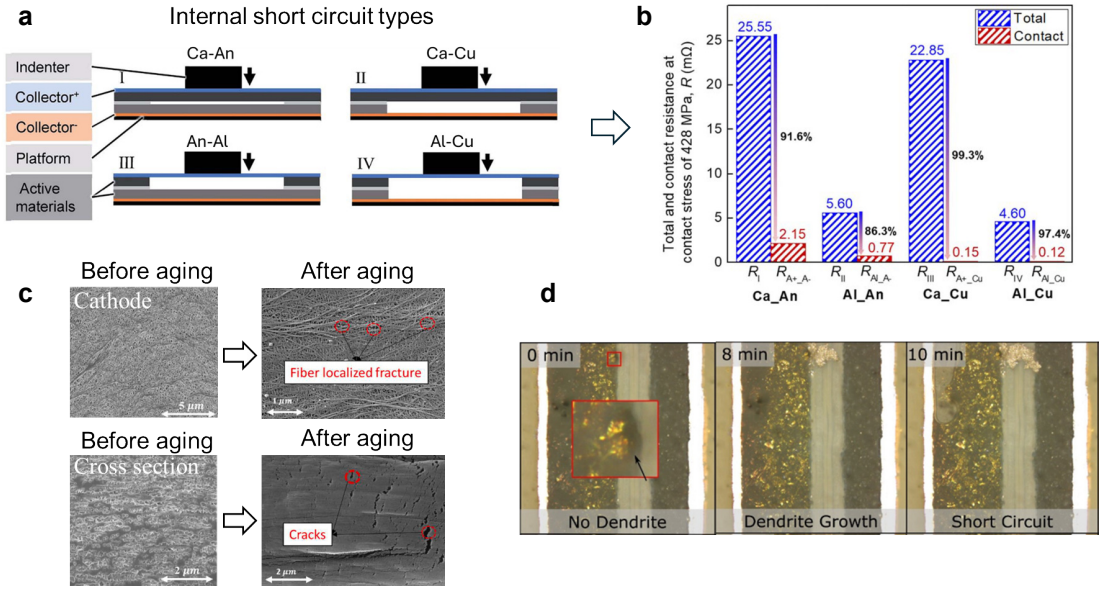

Figure 5 (a) Schematics of different types of ISC: Ca–An, Al–An, Ca–Cu, and Al–Cu. Adapted with permission from Ref. [110] ©2018, Royal Society of Chemistry. (b) Distinguish contact resistances for different ISC types at contact stress of 428 MPa. Reproduced with permission from Ref. [109] ©2022, The Electrochemical Society ("ECS"). (c) Separator mechanical degradation after aging cycling. Adapted with permission from Ref. [111] ©2023, Elsevier Ltd. (b) Direct observation of ISC triggered by lithium dendrite. Adapted under the CC BY 4.0 license from Ref. [112] ©2022, The Authors.

lithium deposition does not necessarily lead to ISC because the metallic lithium can react with the electrolyte to form a SEI or "dead lithium", thereby transforming into irreversible lithium loss[127,128]. Of course, such degradation may not trigger the immediate safety issue but have raised safety concerns in the long term. Therefore, lithium plating is regarded as one of the most dangerous reactions of aging.

Smith et al.[40] found that reductive production of electrolytes (e.g., SEI film) may cause local stress and deactivate the separator by blocking pores. Such pore closure can reduce the ionic transportation rate and promote lithium plating. After triggering ISC, a fusing phenomenon may happen that the local high current passing through the lithium dendrite could heat the dendrite to over 180°C, which melts the tip of the lithium dendrite, thus cutting down the ISC process. This phenomenon is also reported in another work[129]. Hogrefe et al.[112] experimentally studied three lithium deposition under three conditions: (1) lithium deposition without ISC, (2) ISC by Li dendrite growth at the electrode edge, and (3) ISC by Li metal deposition due to blocking of the separator pores. Their studies illustrate the process of lithium dendrite growth during charging-discharging cycles and the subsequent triggering of ISC (Fig. 5d). Additionally, copper (Cu) plating resulting from over-discharging can pierce the separator and induce ISC, similar to lithium plating[130].

3.2 Swelling and rupture of the battery casing

As mentioned in Section 2, battery aging is accompanied by SEI formation and gas generation, leading to deformation and swelling of the battery casing. Two major contributors for the swelling of the cell during aging, i.e., (1) the anode and (2) gas generated due to the side reactions[131,132]. Deformation can be reversible and irreversible. Reversible deformation refers to the deformation due to lithiation. During cycling, graphite can expand 7%−12% due to lithiation[133,134]. Especially, volume expansion of silicon-based materials can achieve 300%[135]. On the contrary, a smaller volume change is observed on the cathode during cycling (e.g., NCA 5%, NCM 1%−2%); on the other hand, irreversible deformation is mainly related to battery degradation (e.g., SEI formation and gas generation). A 10% thickness increase is assigned to SEI growth after aging to 60% SOH[136]. Mohtat et al.[137] observed an irreversible deformation up to 12% at 70% SOH after cycling under −5°C due to lithium plating. Besides, during cycling, the decomposition reactions of SEI are activated (especially under high SOC and in overcharge conditions)[131,138]. After SEI decomposition, new SEI layers form on the interphase of anode and electrolyte, generating large amounts of gas composed of H_2, CO, CH_4, CO_2, C_2H_4[127,132,139,140]. Gas generation inside the battery can build up pressure and deform the battery casing and could lead to the rupture of the casing even with the safety valve design[126]. Gas generation is the major deformation resource of high-temperature aging. It is reported that the thickness of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Graphite battery can increase by 33.54% after 200 cycles due to gas generation[115]. Researchers have investigated the gas pressure inside the battery under different cycling conditions, where SOH, SOC, and temperature are the main factors[141,142]. Schmitt et al.[143] found that the gas pressure irreversibly increases as SOH decreases, i.e., the internal gas pressure can achieve more than 40% of initial pressure at 10% capacity degradation. Additionally, high cycling temperatures also promote higher gas pressure. Therefore, the deformation and swelling of the battery can promote battery degradation and even lead to the casing rupture and battery failure.

4 Aged battery safety behavior under abuse scenarios

Thermal runaway is a phenomenon of abnormal temperature increase in a battery due to internal electrochemical reactions. When the temperature of a cell reaches a specific temperature point, TR occurs, causing the temperature to continue rising autonomously, potentially leading to fire and explosion[144]. Generally, this self-sustaining temperature increase is triggered when the separator reaches its decomposition temperature (e.g., ~130°C depending on the separator material)[145], where the ISC is triggered. Furthermore, ISC can induce a large amount of Joule heat and lead to exothermal decomposition reactions (side reactions) in anode, cathode, and electrolyte materials. As such, multiple exothermal reactions are stimulated within a short time, leading to a drastic temperature rise.

TR could be triggered by three types of abuse: mechanical abuse, thermal abuse, and electrical abuse[105]. Mechanical abuse refers to the abnormal mechanical stress applied on batteries, including penetration, crush, and indentations. This stress can cause failures in electrodes and separators, leading to ISC and subsequently triggering TR[146]. Electrical abuse, including overcharge and over-discharge, also experiences severe ISC, which may lead to metal plating and side reactions[9]. Thermal abuse is the most straightforward triggering method for TR, where the battery is heated by an external or internal heat source, leading to the self-heating thermal decomposition of components. The battery suffering from TR may release flammable gas and experience a dramatic temperature rise, even fire or explosion.

Battery safety behavior under the abuse scenarios

mentioned above has become mandatory tests before entering the market. Most manufacturers focus on the safety behavior of fresh batteries. However, aged batteries exhibit different failure behaviors compared to fresh batteries due to internal structural and chemical changes. It is critical to have a comprehensive understanding of battery safety behavior throughout its lifetime. This section will compare the difference between fresh and aged batteries responding to abuse scenarios to elucidate the role of each aging mechanism in battery failure.

4.1 Thermal abuse

The failure mechanisms of thermal abuse have been extensively studied by many researchers. It has been concluded that the joule heat and heat released from side reactions are the primary sources of temperature rise[147,148].

4.1.1 Thermal runaway triggered by thermal abuse

When the temperature is elevated to a specific point, exothermal chain reactions accelerate. These reactions refer to a process where the initial exothermic reaction triggers subsequent reactions, leading to an increasing number of reactions as the TR progresses, ultimately causing an irreversible temperature rise. For LIBs, the first self-heating exothermic reaction begins with the decomposition of the SEI. In NCM/Graphite electrodes and polyethylene-based ceramic-coated separators, this reaction typically occurs between 85°C and 105°C[149]. This temperature is also mentioned as the onset temperature of self-heating T_{onset}. As decomposition reactions occur, additional reactions are initiated, causing the battery temperature to increase gradually. When the temperature increases to around 120°C, the polyethylene separator starts to melt, leading to a small and localized short circuit (i.e., micro ISC). A rapid temperature increase is observed at T_{TR} (230°C), where the separator breaks down completely, resulting in a full ISC. T_{TR} is also defined as the trigger temperature of TR, beyond which the temperature increases dramatically and irreversibly. T_{onset}, T_{TR} are corresponding to the thermal stability of the battery, indicating the point at which the battery begins to enter thermal runaway. T_{max} refers to the maximum temperature that the TR process can achieve, after which the cell starts to cool due to the exhaustion of electrochemical energy and heat dissipation to ambient. T_{max} is generally used to evaluate the destructive potential of TR. Since T_{onset}, T_{TR} and T_{max} represent three temperature milestones during the TR process, they are regarded as characteristic temperatures of TR. Note that these characteristic temperatures can vary for different battery material systems due to the varying thermal stability of the materials.

4.1.2 Aging influence

Low temperature cycling and fast charging lead to a decrease in onset temperature T_{onset} and trigger temperature T_{TR} (Table 1). Severe lithium plating is often observed when the battery cycles under low temperatures or high charging currents[157–159]. Metallic lithium dendrites are highly reactive and can participate in exothermic reactions at relatively low temperatures[157]. Reactions between metallic lithium and electrolyte can release enough heat to trigger thermal runaway[159]. Wu et al.[160] prepared aged

Table 1 Aging influence on overheating-induced TR

Material	Aging methods	Temperature (°C)	C-rate (C)	SOH (%)	T_{onset} (°C)	T_{TR} (°C)	T_{max} (°C)	Reference
NCM+LMO/Graphite	Cycling	−10	0.1	86–95	55–75 ↓	170–190 ↓	650–710 →	[150]
NCM/Graphite	Cycling	−5	1	75–100	50–70 ↓	190–210 ↓	810–850 →	[51]
NCA/Graphite	Cycling	0	0.5	70–80	36–70 ↓	123–160 ↓	450–700 ↓	[151]
NCM/Graphite	Cycling	20	1	70–90	70–80 ↓	214–221 →	–	[152]
NCM/Graphite	Cycling	25	2	75–100	60–70 ↓	190–210 ↓	500~810 ↓	[51]
NCM/Graphite	Cycling	45	1	70–90	95–105 ↑	214–221 →	–	[152]
LFP/Graphite	Cycling	50	WLTC, 1, 2	–	–	–	315 →	[153]
NCM/Graphite	Cycling	50	WLTC, 1, 2	–	195 ↓	226 ↓	660 ↓	[153]
NCM/Graphite	Cycling	55	1	75–100	65–70 →	210–220 →	810–850 →	[51]
NCM/Graphite	Storage (100% SOC)	55	–	75–100	70–100 ↑	210–220 →	810–850 →	[51]
LMO	Storage (100% SOC)	55	–	60–100	110–150 ↑	178–195 ↑	–	[154]
NCM+LMO/Graphite	Storage (100% SOC)	60	–	60	70 ↓	120 →	350 ↓	[59]
LFP/Graphite	Storage	60	–	70, 90	92, 83 ↑	145, 147 ↑	–	[155]
NCM+LMO/Graphite	Suspension overheating	80–110	–	50–90	60–120 ↑	190–210 ↑	600–700 ↓	[150]
NCM/Graphite	Slight overcharge	–	0.5	70	105 ↓	143 ↓	667 ↓	[156]
NCM/Graphite	Slight over-discharge	–	0.5	–	59–79 ↓	170–173 ↓	441–519 ↓	[92]

Note: → refers to similar value compared with fresh cell; ↑ refers to increasing trends compared with fresh cells; ↓ refers to decreasing trends compared with fresh cells; – refers to no reports in the paper. LFP, $LiFePO_4$; LMO, $LiMn_2O_4$; NCA, $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$; NCM, $LiNi_{1-x-y}Mn_xCo_yO_2$; SOC, state of charge; SOH, state of health; WLTC, battery cycling configuration of the Worldwide harmonized Light vehicles Test Cycles.

$LiCoO_2$/Graphite cells by 2C cycling at −10°C and triggered to TR in an EV+Accelerating Rate Calorimeter (ARC) by the overheating method. They observed a decrease in the thermal runaway triggering temperature T_{TR} of aged cells. SEM, X-ray photoelectron spectroscopy, and electrochemical impedance spectroscopy characterized the lithium plating on the anode, which proved to be the source of the decrease in thermal stability.

Conversely, high-temperature cycling is reported to improve the thermal stability of batteries due to the increased thickness of the SEI layer during the aging process. As SEI thickness increases, more lithium and electrolytes are consumed on the anode, reducing the heat release in electrolyte and anode decomposition reactions. Therefore, SEI growth can increase both the onset temperature T_{onset} and triggering temperature T_{TR}[149]. Borner et al.[152] prepared aged cells by cycling under 45°C. The aged cell is then triggered to thermal runaway by the overheating method in an EV+ARC. The test results indicate there is an increase of T_{onset} for high-temperature aging batteries than fresh cells. To evaluate lithium plating on the anode, Li magic angle spin nuclear magnetic resonance spectroscopy was used, indicating no lithium plating when cycling at 45°C. Thermogravimetric analysis and pyrolysis–gas chromatography–mass spectrometry analyzed the thermal stability of the aged anode, showing that battery aging increases the SEI layer thickness. This results in more embedded electrolyte components and their decomposition products, leading to higher thermal stability of the anode. However, it was also reported a decrease of T_{onset} and T_{TR} after high-temperature cycling with lithium plating due to localized drying of electrolyte[153,161]. Therefore, the aging effect under high temperatures still requires further understanding.

Additionally, the influence of fast charging on battery aging has been extensively studied[51,159,162,163]. Fast charging promotes the formation of metallic lithium dendrites, which affect the thermal hazard performance of aged batteries. Lithium dendrites formed during the fast-charging process can react with the electrolyte at relatively lower temperatures. The energy released by this exothermal decomposition reaction results in a reduction of T_{onset}[159], thereby decreasing the thermal stability. Li et al.[159] charged battery by using 1.5C and 3C fast charging methods, which results in aged batteries with approximately 85% capacity retention. These aged batteries were then subjected to thermal runaway by overheating. The results indicate that with elevated charging rates, both the T_{onset} and T_{TR} decreases. Therefore, the thermal stability of fast-charging-induced aged batteries is further deteriorated (Fig. 6a). Aged cell components were disassembled and tested by differential thermal analysis (DSC). The anode with electrolyte under 3C charging rate demonstrates an extremely high peak a during 100°C and 200°C (Fig. 6b). After the surface component was scratched off, the peak almost disappeared, indicating that the scratched components (Fig. 6c) were primarily composed of lithium plating. Therefore, lithium plating has been proven to be the main factor in the thermal stability variation of fast-charging aged batteries.

Overcharging-induced aging would reduce the thermal stability of the battery by inducing the phase transition of the cathode crystal structure. Besides, a switch of electrode heat contribution ratio during thermal runaway can be observed for overcharged batteries, from the majority of the cathode (≥ 80%) at 120% SOC to anode dominance (around 60%) at 140% SOC[164]. In addition, overdischarging aged batteries have lower T_{onset} and T_{TR} due to the lower thermal stability of regenerated SEI[92]. Besides, Ren et al.[51] studied the thermal behavior of high-temperature calendar aging batteries and proved that calendar aging increases SEI thickness and significantly improves thermal stability. Therefore, the aging path can influence TR behavior in different ways corresponding to the dominant side reactions under each scenario (Fig. 7).

4.2 Mechanical abuse

4.2.1 Aging influence on battery mechanical properties

Mechanical properties govern the mechanical integrity and safety of the cells upon both internal and external stresses. As discussed in Section 2, ISC can be triggered by the failure of components (especially the separator). Aging-induced side reactions modify the mechanical properties of the anode, cathode, and separator, altering the material failure sequence and leading to different ISC modes (Fig. 8). Side reactions can induce an aging effect on battery components (e.g., anode thickening, separator degradation), leading to changes in material-level and cell-level mechanical properties. Tensile and compression experiments are the most representative tests for studying mechanical properties. It is reported that aged graphite-based anodes exhibit a lower strength, smaller failure strain, and Young's modulus compared to the fresh anodes both in tensile and compression tests (Fig. 9b), which may be caused by the anode thickening due to SEI growth[166,169]. Besides, secondary SEI induced by lithium plating can also increase anode thickness[165]. It is reported that cracks and electrolyte decomposition on an anode can lead to anode shrinkage and reduce material connectivity, which causes a lower anode strength[170]. Several studies reported that no obvious or small difference between the stiffness of aged versus fresh cathodes is

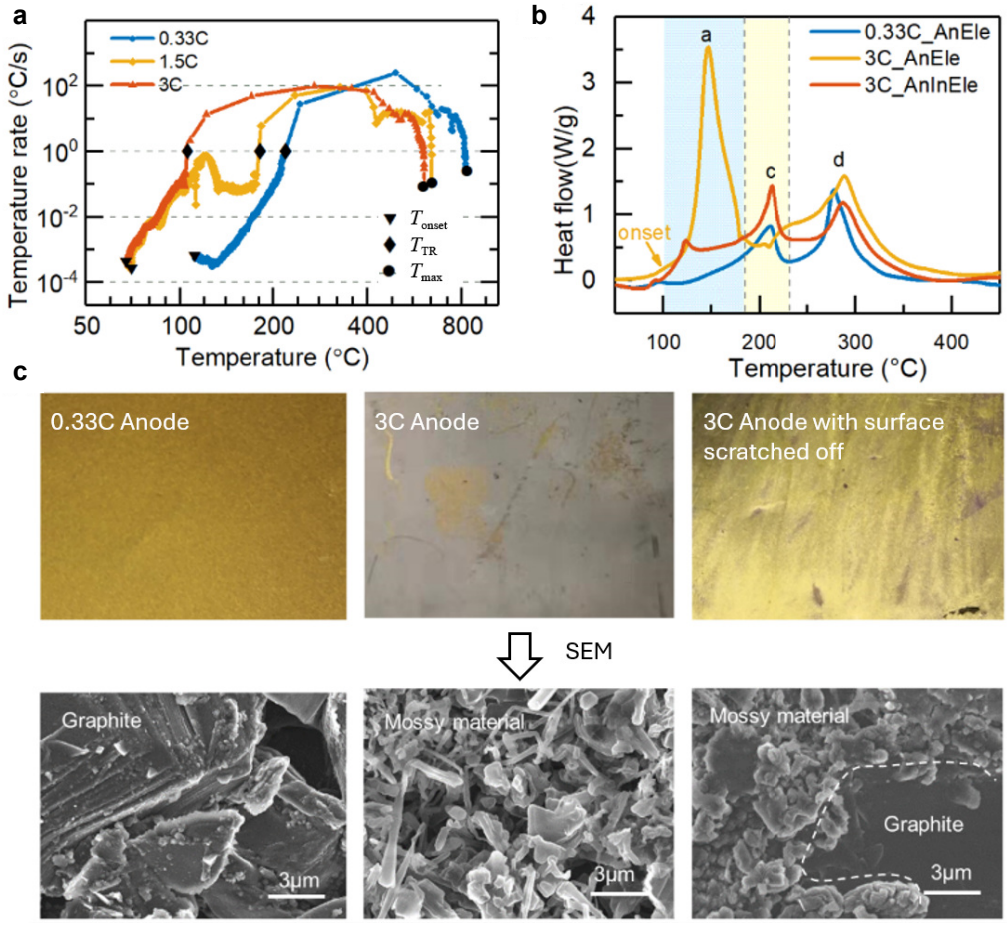

Figure 6 (a) Thermal runaway temperature rate variate with temperature by different charging rates 0.33C, 1.5C, and 3C. (b) DSC heat flow of anode powder mixed with electrolyte with exothermic reactions represented by peak a, c, and d. AnEle refers to anode powder with electrolyte. AnlnEle is a mixture of electrolyte and anode with surface scratched off. (c) Optical photos and SEM images of anode aging with different charging rates 0.33C and 3C. Adapted with permission from Ref. [159] ©2019, American Chemical Society.

observed[166,167], which also proves that battery aging mainly introduces reactions on the anode. As for the separator, the stress-strain curve of tensile tests demonstrates a significant dependency on the aging state. The responsible reason is that cycling-induced stress damages the separator crystal structure and pore closure, thus changing the mechanical properties of the separator. The maximum tensile strength of the aged separator can be reduced to 50% of the fresh one[167]. Compared with the results of separator tensile tests, the stress value of compression tests of aged batteries slightly increases. Since the compression test is loaded from the out-of-plan and does not affect the weakest points of pores, less aging influence is observed in the compression scenarios. Therefore, electrochemical aging influences the mechanical performance of battery materials. Reversely, a mechanical defect in the battery components during the manufacturing process can severely accelerate the aging process due to the damage to electrochemical connectivity[170].

Furthermore, aging influence on material-level properties further impacts the stiffness of integrative batteries (cell-level) is reported. Stiffness of both quasi-static and dynamic out-of-plane direction indentation tests of aged cells decrease due to the anode thickness increase, i.e., lithium plating, accumulation of plastic deformation, and SEI thickening due to cracking (Fig. 9a)[165,171]. For the in-plane direction indentation of punch cells, aged batteries have a smaller buckling area compared with fresh cells at the same deformation condition, which is also caused by anode thickness change. A deeper voltage drop can be observed for aged batteries during indentation tests, resulting from the decrease in mechanical strength of the separator[172].

4.2.2 Aging influence on mechanical-abuse-induced thermal runaway

Based on the findings of the current study, aged batteries exhibit less intense thermal runaway performance when triggered by mechanical abuse, showing the following behaviors: (1) more abusive loading and deformation of batteries are required to trigger TR; (2) the TR triggering time of batteries is delayed; (3) the rate of temperature rise; and (4) TR is exacerbated by lithium plating.

The battery aging demonstrates a decrease in fail-

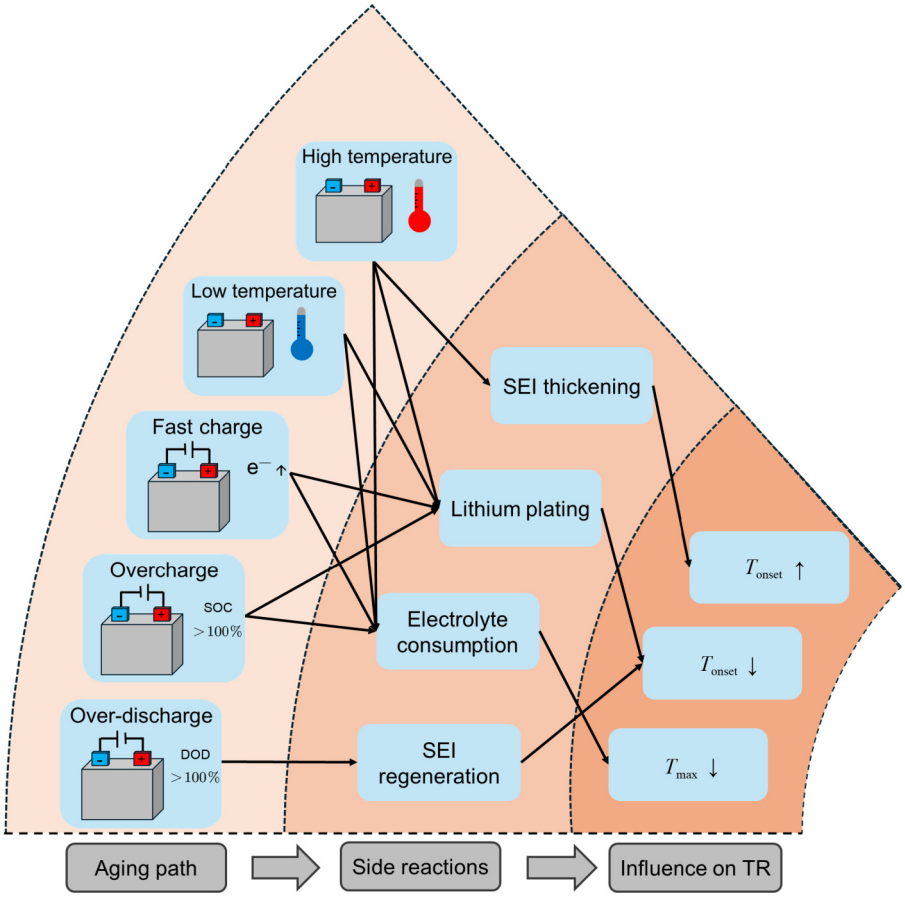

Figure 7 A summary of the major aging path along with dominant side reactions and influence on TR.

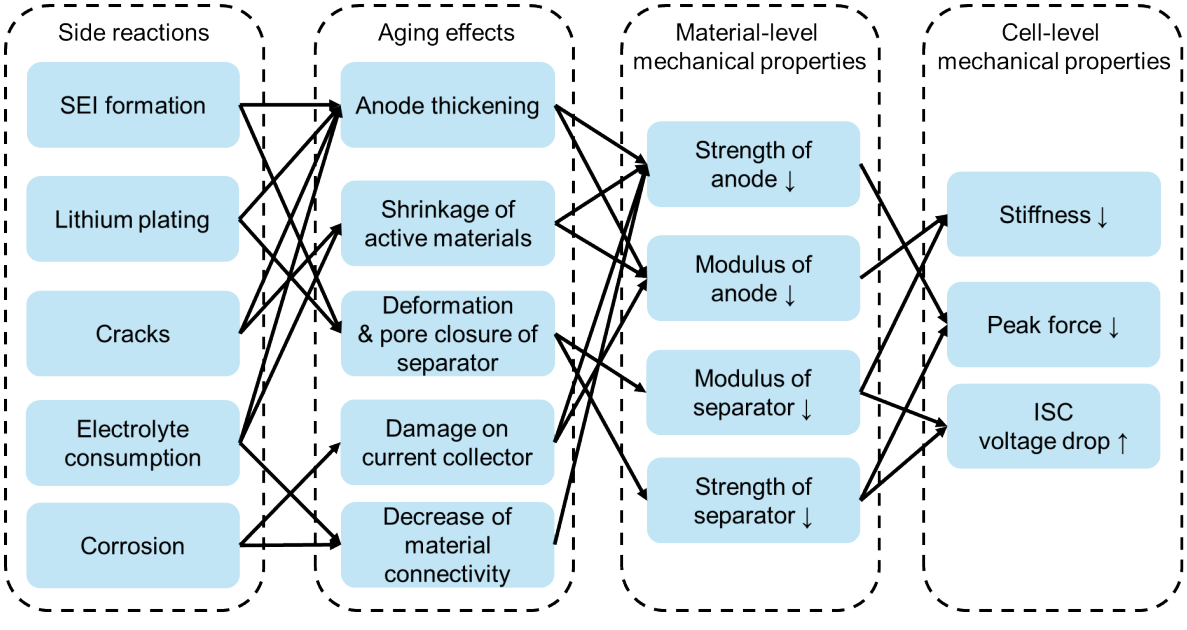

Figure 8 A summary of the aging effect on battery mechanical properties

ure loading, displacement, and voltage, with a lower battery Young's modulus[146]. Kovachev et al.[173] cycled the NCM-LMO/Graphite battery under 60°C and 1C for 700 cycles to prepare aged batteries. A quasi-static indentation test was applied to these batteries until mechanical failure, indicating that the failure loading and impactor displacement of aged batteries can be enhanced by 30% and 26%, respectively. This improvement is attributed to the increased thickness of the SEI and separator. Furthermore, the decrease in temperature rate during thermal runaway can be attributed to limited lithium-ion intercalation caused

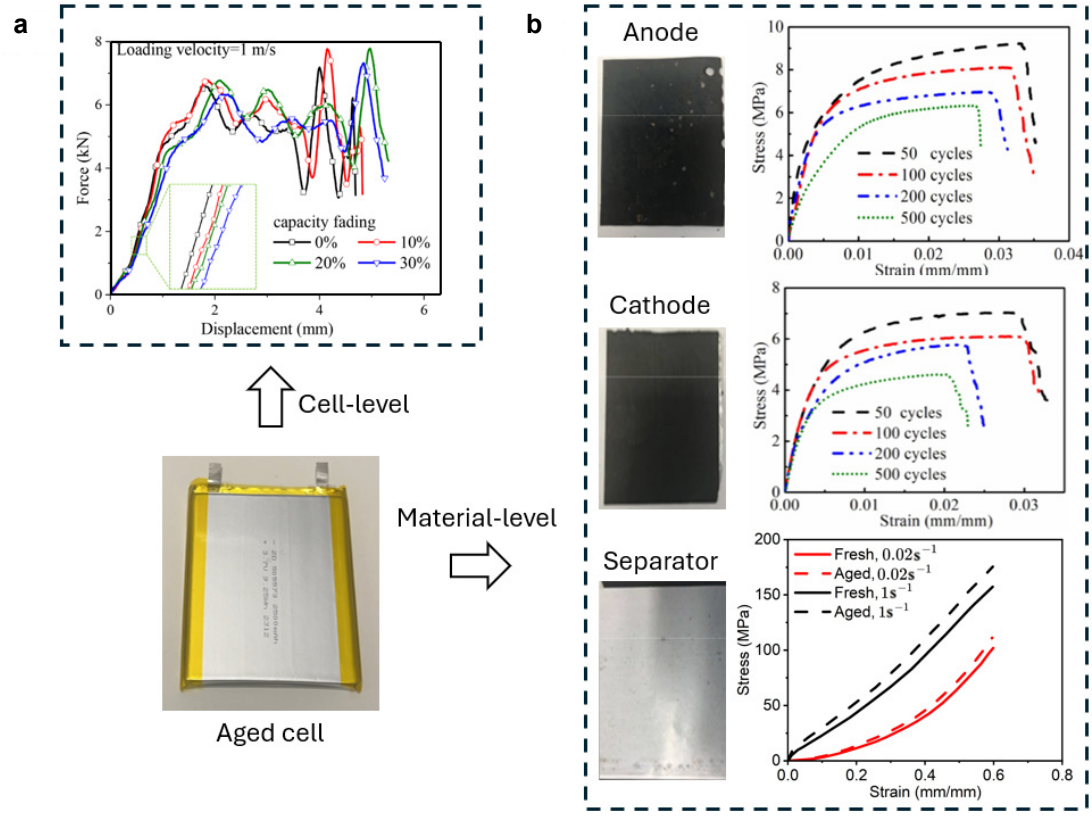

Figure 9 Effect of aged batteries. (a) Cell-level force responses with a different aging degree. Reproduced with permission from Ref. [165] ©2022, Elsevier Ltd. (b) Materials-level force responses with a different aging degree[166–168]. Adapted with permission from Ref. [166] ©2017, IOP Publishing Ltd. Reproduced with permission from Ref. [168] ©2020, Elsevier Ltd.

by SEI growth and electrolyte decomposition[146,174]. The aging effect can delay the triggering time of thermal runaway after penetration tests due to insufficient joule-heat during ISC to heat the battery to T_{TR}[157].

On the other hand, the battery TR stability is weakened by Li plating during indentation tests. Low-temperature (0°C) cycling aged batteries can sustain larger deformation before the ISC is triggered[151]. However, the ISC behavior is more violent due to a larger ISC area (caused by the larger deformation) as well as Li plating caused by low-temperature cycling, where a faster voltage drop, and higher T_{max} can be observed[165]. The time intervals between ISC and TR triggering become smaller. Therefore, further understanding of the aging effect on battery mechanical-abuse-induced thermal runaway is required. Collectively considering the mechanical and thermal behavior of aged batteries under mechanical abuse, the overall safety of aged cells is surprisingly better than fresh cells.

4.3 Electrical abuse

Electrical abuse mainly includes overcharging, over-discharging, and external short circuits (ESC). In the previous chapters, we discussed the side reactions that occur during slight overcharge and over-discharge. More severe reactions arise as the conditions deteriorate further, finally triggering thermal runaway. Overcharging occurs when the electrical energy charged into a battery exceeds its maximum capacity, causing the voltage to rise above the nominal level until a thermal runaway is triggered. Overcharging can promote side reactions such as Li plating, transition metal dissolution, and electrolyte decomposition. In contrast, over-discharge is to discharge the battery excessively. Over-discharging leads to copper deposition on the anode, which may penetrate the separator and cause an internal short circuit. Additionally, ESC refers to using a small resistance conductor to connect the anode and cathode, which will generate a large current.

4.3.1 Thermal runaway triggered by electrical abuse

The failure mechanisms of overcharge abuse have been extensively studied, concluding that joule heat and heat released from side reactions are the main sources of temperature rise[147,148]. SOC represents the remaining capacity available in a battery at a given time, and typically, the voltage has a quantitative correlation with SOC[175]. Overcharge-induced TR can be summarized based on the SOC range starting from SOC > 120% (Fig. 10a)[176]:

(I) 120% < SOC < 140%. Transitional metal (e.g., Mn^{2+}, Fe^{2+}) dissolution is strengthened due to the

high potential on the cathode. The anode has no capacity for more Li^+ intercalation, and there is lithium deposition on the surface of the anode[178]. Deposited lithium and transitional metal ions react with the solvent, forming more SEI, which will increase the internal resistance of cells. Therefore, in this regime, joule heat and side reactions are the main reasons for the temperature rise.

(II) 140% < SOC < 160%. As the voltage increases, highly delighted cathode materials become unstable and react with the electrolyte under high potential, generating gas and heat[179,180], leading to swelling. Simultaneously, the temperature reaches the decomposition temperature of SEI, triggering exothermal chain reactions[177].

(III) SOC > 160%. Battery rupture occurs due to the high internal pressure. Heat accumulation and increased temperature induce further exothermal chain reactions. The separator collapses under the high temperature, leading to a large-scale ISC. The temperature dramatically increases to the maximum temperature, and all the energy inside the battery will be released instantly, which depletes the voltage completely in a short time. The battery failed and can only be regarded as a resistor[181].

On the other hand, the over-discharging process has been identified by three stages (Fig. 10b)[177]. As DOD deepens (DOD > 110%), copper dendrites generate on the cathode surface, penetrating the separator and causing an internal short circuit. The voltage dramatically decreases to 0 V, and the cell fails.

4.3.2 *Aging influence*

The aging effect on overcharge-induced TR has been extensively researched. No bursting is observed for aged batteries with SOH ≤ 80% and charge C-rate ≤ 1C, indicating a smaller thermal hazard. The T_{onset} of TR decreases first and then increases as SOH decreases, which may be caused by the combined effect of lithium plating produced SEI (promotion of TR) and loss of active materials (suppression of TR)[178]. Yuan et al.[182] investigated the overcharge-induced TR behavior of high-temperature-aged LMO/Graphite batteries with SOH at 87%, 81%, and 75%. A delay in TR triggering time can be observed as SOH decreases due to the lithium plating and transitional metal dissolution. However, the time interval between self-heating onset and TR triggering significantly decreases (51 s) compared to fresh cells (118 s) due to more lithium deposition. On the other hand, the overcharge-induced TR behavior of fast-charge-aged batteries was studied, which shows a decreased trend of TR triggering time[183]. This phenomenon is caused by the early occurrence of lithium plating due to the degradation of the anode, which can hold less capacity. Therefore, the overcharge-induced TR behavior may change due to the aging method, materials system, and test configuration.

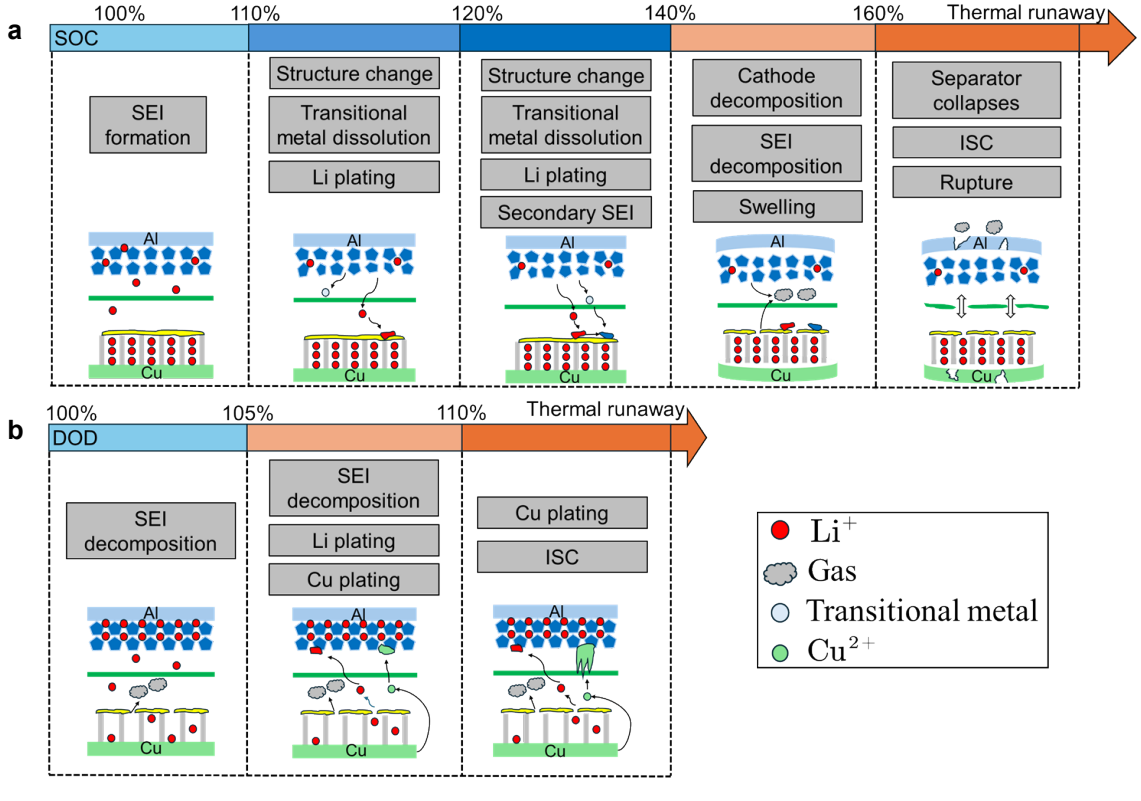

Figure 10 (a) Schematic of overcharge-induced thermal runaway[176]. (b) Schematic of over-discharge-induced thermal runaway[177].

Compared with overcharging, over-discharging has been relatively less reported. Qian et al. investigated aged battery thermal runaway by an over-discharging method. The battery is cycled with a 2C high current rate under ambient temperature. The test results indicated that as the aging degree increases, the temperature rising rate increases, and triggering time becomes early. There is also an increase in the maximum temperature. Therefore, the authors argue that aging decreases the thermal stability[177].

ESC-induced TR can rarely happen during the application of commercial batteries due to the existence of fuse protectors, thus drawing less attention. Some works investigated aged cell ESC-induced TR by using the copper cable with low resistance to physically connect the anode and cathode[184,185]. No aging effect is observed for ESC scenarios. An increase in cell temperature can be observed (around 100°C) but no further thermal runaway is happening. Compared with ISC, ESC generally has less resistance due to a wider contact area between the electrodes, generating less joule heat.

4.4 Thermal runaway propagation and gas emissions

A single-cell TR can propagate via heating the surrounding cells, i.e., thermal runaway propagation (TRP). TRP can be influenced by multiple factors (i.e., single-cell heat generation, cell-to-cell heat resistance, heating power, etc.)[186–188]. While numerous studies have examined the impact of module and pack design on TRP, limited research has focused on TRP in aged batteries. Zhao et al.[189] investigated the TRP behavior of an aged battery module after cycling at low temperature (−10°C). The findings indicated that battery aging reduced the average heat transfer between cells during TRP, potentially increasing the risk of thermal runaway. Additionally, maximum temperature, mass loss, and voltage drop for each cell were influenced by the electrical connection methods, although no clear trends were observed. Therefore, further research is needed to explore the effects of aging on TRP, particularly in relation to aging history, battery materials, and module/pack designs.

As mentioned in previous sections, fire and gas emissions often accompany the TR process, posing additional safety concerns. It is reported that battery fires are linked to the flammability of electrolyte and gas release, which can ignite when exposed to high temperatures[190]. Therefore, studying gas emissions provides valuable insights into hazards beyond heat accumulation from internal side reactions. During TR, battery emissions primarily consist of HF, CO, H_2, CO_2, C_2H_4, and CH_4[191,192]. Aging-induced material changes can affect both the volume and composition of gases. Gas composition can be influenced by decay and regeneration of the SEI layer[193]. Most aged cells emit 10% more H_2 and CO, which is flammable and toxic. The amount of C_2H_4, reduces with a decrease in SOH due to the consumption of ethylene carbonate electrolyte. Additionally, an aging history-related gas evolution has been reported with C_2H_2 observed only in batteries aged through high-temperature storage, likely due to the degradation of the electrolyte and formation of C_2-hydrocarbons. On the other hand, the total volume of gas released by aged batteries decreases with the degree of aging process[191].

4.5 Aging battery thermal runaway modeling

Thermal runaway modeling has been applied by researchers to gain a deeper understanding of decomposition reactions inside the battery during the TR process. Key decomposition reactions considered in TR models include SEI decomposition, anode–electrolyte reaction, cathode–electrolyte reaction, and electrolyte decomposition[194]. The total heat generation rate due to decomposition reactions can be calculated as:

$$q_{total} = q_{SEI} + q_{an} + q_{ca} + q_e \tag{12}$$

$$q_x = m_x \Delta H_x R_x \tag{13}$$

where, x denotes reactants (i.e., SEI, anode, cathode, and electrolyte). m_x refers to volumetric mass proportion of each reactant. ΔH_x is the reaction enthalpy. The reaction rate of each reaction R_x can be expressed in Arrhenius equations[195]:

$$R_{SEI} = -\frac{dc_{SEI}}{dt} = A_{SEI} \exp\left(-\frac{E_{a,SEI}}{RT}\right) c_{SEI} \tag{14}$$

$$R_{an} = -\frac{dc_{an}}{dt} = A_{an} \exp\left(-\frac{E_{a,an}}{RT}\right) \exp\left(-\frac{t_{SEI}}{t_{SEI,0}}\right) \tag{15}$$

$$R_{ca} = -\frac{d\alpha}{dt} = A_{ca}\alpha(1-\alpha) \exp\left(-\frac{E_{a,ca}}{RT}\right) \tag{16}$$

$$R_e = A_e \exp\left(-\frac{E_{a,E}}{RT}\right) c_e \tag{17}$$

where, c_x is dimensionless concentration of reactant x. A_x refers to pre-exponential factor and $E_{a,x}$ is activation energy. t_{SEI} is thickness of SEI, which is consumed during TR and deducted from initial value $t_{SEI,0}$. α denotes the degree of conversion for the cathode material.

Few researchers have focused on modeling the effect of aging on TR. SEI formation and lithium-ion plating are considered the most critical aging reactions influencing TR behavior. As discussed earlier, SEI thickening enhances TR stability. Abada, et al.[155] developed a thermal runaway model for aged cells,

where SEI formation was identified as the primary driver of capacity loss. Thickness of SEI increases with degradation of SOH:

$$t_{\mathrm{SEI},0} = t_{\mathrm{SEI,fresh}} + \frac{M_{\mathrm{SEI}}}{\rho_{\mathrm{SEI}} S_{\mathrm{n}}} C_{\mathrm{loss}} \frac{1}{2F} \tag{18}$$

where, $t_{\mathrm{SEI},0}$ denotes the initial thickness of aged batteries, which is further transferred to Eq. (13), thus impacting the TR process. $t_{\mathrm{SEI,fresh}}$ is SEI thickness of fresh batteries. M_{SEI} denotes to the molar mass. ρ_{SEI} is density of the SEI film. S_{n} is the electroactive surface of the anode. Faraday's law was used to express SEI formation amount as a function of capacity loss, $n_{\mathrm{SEI}} = \frac{C_{\mathrm{loss}}}{2F}$. C_{loss} is capacity loss in the battery.

Lithium plating is considered a key factor in the early triggering of thermal runaway, especially in aging processes during low-temperature and fast charging cycles. Zhao et al.[195] built a TR model that accounts for capacity degradation due to lithium plating, where it is regarded as the only source of capacity loss.

$$c_{\mathrm{Li},0} = \frac{C_{\mathrm{loss}}}{C_{\mathrm{initial}}} = 1 - \mathrm{SOH} \tag{19}$$

in which, $c_{\mathrm{Li},0}$ denotes dimensionless initial concentration of plated lithium. Plated lithium can react with electrolyte at around 180°C and generate a large amount of heat[196]. Therefore, the reaction rate of lithium-electrolyte is added to the model as:

$$R_{\mathrm{Lie}} = -\frac{\mathrm{d}c_{\mathrm{Li}}}{\mathrm{d}t} = A_{\mathrm{Lie}} \exp\left(-\frac{E_{\mathrm{a,Lie}}}{RT}\right) \frac{k_{\mathrm{Li}} c_{\mathrm{Li}}}{1 + k_{\mathrm{Li}} c_{\mathrm{Li}}} c_{\mathrm{e}} \tag{20}$$

where, k_{Li} is a proportion factor for the metal lithium/electrolyte reaction. A_{Lie} and $E_{\mathrm{a,Lie}}$ are kinetic parameters for Arrhenius equations, which can be calculated through DSC tests[197]. Specifically, the plated lithium can consume solvents in the electrolyte, which couples to the electrolyte concentration:

$$\frac{\mathrm{d}c_{\mathrm{e}}}{\mathrm{d}t} = -R_{\mathrm{e}} - k_{\mathrm{ele}} R_{\mathrm{Lie}} \tag{21}$$

in which, k_{ele} denotes a stoichiometry for lithium/electrolyte reaction.

5 Summary and outlook

5.1 Summary

Batteries face critical safety issues that hinder the widespread application of LIBs. The influence of aging on the performance and safety of LIBs is inevitable during their usage. This paper provides an overview of battery aging mechanisms and their influence on battery performance and safety. Battery aging mechanisms are identified by operational behavior and categorized into cycling aging and calendar aging. Specific aging paths, such as temperature, SOC, and cycling current, are correlated to various aging mechanisms. Extreme cycling and storage conditions, such as high or low temperature, high SOC, high charging current, overcharge, and overdischarge, can accelerate the aging process.

Furthermore, safety issues during the battery aging process are identified, with particular emphasis on ISC and the swelling or rupture of the battery casing, which can potentially lead to thermal runaway, fires, and explosions. The impact of aging on safety problems under abuse scenarios is also investigated. Among the various aging mechanisms, lithium plating and SEI growth are proven to have the most substantial impact on thermal runaway behavior. The thermal hazard characteristics of aging batteries are introduced, and the TR behaviors of aging batteries are summarized based on the triggering method (thermal, mechanical, and electrical). A dependency of aging paths on TR behavior is identified, which could be related to fundamental aging reactions such as lithium plating and SEI thickening.

Additionally, the influence of battery aging on TRP and gas emissions is discussed, highlighting safety concerns following the initiation of thermal runaway. Modeling studies of thermal runaway in aged batteries are also examined, providing valuable insights into the role of aging reactions—such as SEI formation and lithium plating—on the thermal runaway behavior of aged cells.

5.2 Challenges and opportunities

5.2.1 Research challenges

Although extensive research has been conducted on aging battery thermal hazards, further investigation is still required in many extended areas. Several key questions remain for further understanding.

(1) Complexity of aging mechanisms. The aging process of LIBs is influenced by a multitude of factors, including temperature, SOC, cycling current, and storage conditions. These factors can accelerate various aging mechanisms and can be identified as SEI growth, lithium plating, and electrolyte decomposition. However, the complexity of these interactions makes it difficult to isolate and study individual aging processes quantitatively, posing a significant challenge for researchers. Besides, a knowledge gap remains regarding scenarios involving multiple aging factors (e.g., high C-rate combined with elevated temperature), which requires further attention.

(2) Knowledge gap between aging reactions and their safety behaviors. Current research has identified several aging reactions that influence safety behaviors, such as lithium plating, which promotes

the onset of thermal runaway. However, many other effects of aging side reactions (e.g., transitional metal dissolution and electrode phase transition) on LIB safety remain unclear and require further investigation.

(3) Lack of standardized testing protocols. There is no universally accepted protocol for testing the aging and safety of LIBs comparably and quantitatively. Different studies use varying methods and conditions, making it difficult to compare results and draw consistent conclusions from various databases. The development of standardized testing procedures is essential for advancing the field and ensuring that findings are reliable and applicable across different contexts.

(4) Predictive modeling difficulties. Creating accurate models to predict battery aging and safety behaviors is challenging due to the numerous variables involved. Existing models often fail to account for all the factors influencing aging, leading to discrepancies between predicted and actual performance. Improving predictive models requires integrating comprehensive data from real-world usage and controlled lab experiments.

5.2.2 *Future opportunities*

Compared to fresh batteries, significant knowledge gaps remain in our understanding of aged batteries (Table 2). However, with the advancement of our understanding and the development of improved characterization techniques, several key opportunities have emerged:

(1) Physical-based TR modeling for aged batteries. Current models typically assume that a single side reaction dominates capacity fading, subsequently influencing TR behavior. However, as our understanding of aging mechanisms improves, incorporating more complex side reactions will enhance our knowledge of the interplay between aging and TR. This could lead to more accurate and predictive models for aged batteries.

(2) TRP in aged batteries. From an engineering application perspective, TRP is a critical concern, particularly for electric vehicles and large energy storage systems. The influence of aging on TRP remains underexplored, with its impact showing a complex correlation with the engineering design of battery modules. Future research should focus on TRP-related temperature behaviors, heat generation, gas ejection, and modeling to better address safety concerns in aged systems.

(3) Advanced quantitative diagnostic techniques. Recent advancements in diagnostic tools, such as *in situ* electron microscopy, X-ray diffraction, and synchrotron, allow for real-time monitoring of battery aging processes at the atomic level. These techniques provide valuable insights into the structural and chemical changes occurring within batteries, paving the way for the development of more effective aging mitigation strategies.

(4) Material innovations. New chemistry and materials for electrodes and electrolytes offer promising opportunities to enhance battery lifespan and safety. For example, solid-state electrolytes can potentially eliminate issues related to liquid electrolyte decomposition and leakage. Similarly, advanced cathode and anode materials with higher stability and capacity can reduce the rate of degradation and improve overall battery performance.

(5) Machine learning and artificial intelligence (AI). The application of machine learning and AI in battery research holds immense potential for accelerating the understanding of aging mechanisms and safety behaviors. As our knowledge of the physics behind aging mechanisms and their impact on battery thermal safety improves, the accuracy of machine learning models, particularly physics-informed AI algorithms (e.g., physics-informed neural networks), is also enhanced. This advancement can accelerate the development of quantitative models that describe battery aging behaviors and provide clearer insights into the status of aging cells.

(6) Regulatory and industry collaboration. Collaboration between researchers, industry stakeholders, and regulatory bodies can drive the development of standardized testing protocols and safety guidelines. Establishing clear regulations and best practices will ensure that batteries meet safety standards and perform reliably throughout their lifespan.

By addressing the complexities of aging mechanisms, enhancing safety protocols, and leveraging advanced technologies, researchers can pave the way for the next generation of durable and safe lithium-ion batteries. Continued innovation and collaboration across the industry will be essential to overcome current obstacles and unlock the full potential of this critical energy storage technology.

Table 2 Comparison of research on fresh and aged cells.

Cell statement	Single-cell TR					TRP				
	Temperature	Heat	Gas	Fire	Modeling	Temperature	Heat	Gas	Fire	Modeling
Fresh	●	●	●	●	●	●	●	●	●	●
Aged	●	●	●	○	○	○	○	○	○	○

Note: The symbol ● indicates extensive research has been conducted in the area, while ○ represents a lack of work in the area. TR, thermal runaway; TRP, thermal runaway propagation.

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Shuguo Sun: Methodology, Data analysis, and Writing – original draft; Jun Xu: Conceptualization, Methodology, Supervision, and Writing – review & editing. Both the authors have approved the final manuscript.

Data availability

All the data has been included in the paper.

Declaration of competing interest

Jun Xu is one of the editorial board members of this journal, but he was not involved in the peer review or decision of this article. The other contributing author reports no conflicts of interest in this work.

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Use of AI statement

None.

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