

All-temperature area battery application mechanism, performance, and strategies

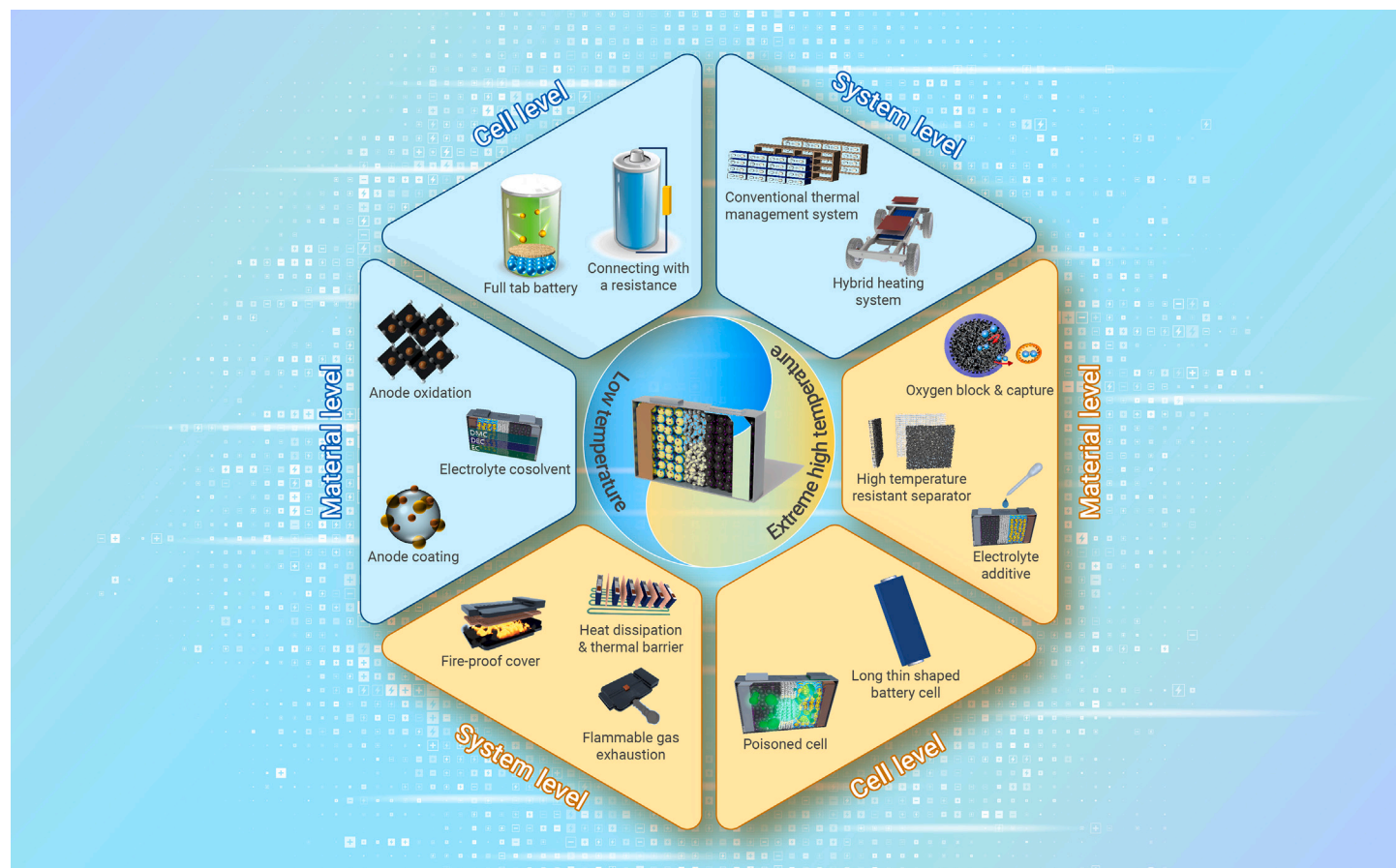
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Mechanism-temperature map reveals all-temperature area battery reaction evolution.
- Battery performance and safety issues are clarified from material, cell, and system levels.
- Strategy-temperature map proposes multilevel solutions for battery applications.
- Future perspectives guide next generation high performance and safety battery design.



All-temperature area battery application mechanism, performance, and strategies

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Further applications of electric vehicles (EVs) and energy storage stations are limited because of the thermal sensitivity, volatility, and poor durability of lithium-ion batteries (LIBs), especially given the urgent requirements for all-climate utilization and fast charging. This study comprehensively reviews the thermal characteristics and management of LIBs in an all-temperature area based on the performance, mechanism, and thermal management strategy levels. At the performance level, the external features of the batteries were analyzed and compared in cold and hot environments. At the mechanism level, the heat generation principles and thermal features of LIBs under different temperature conditions were summarized from the perspectives of thermal and electrothermal mechanisms. At the strategy level, to maintain the temperature/thermal consistency and prevent poor subzero temperature performance and local/global overheating, conventional and novel battery thermal management systems (BTMSs) are discussed from the perspective of temperature control, thermal consistency, and power cost. Moreover, future countermeasures to enhance the performance of all-climate areas at the material, cell, and system levels are discussed. This study provides insights and methodologies to guarantee the performance and safety of LIBs used in EVs and energy storage stations.

INTRODUCTION

The carbon neutrality proposal has promoted clean energy development in recent years.^{1,2} Electric vehicles (EVs) are investigated as the appropriate replacement for the conventional internal combustion engine-based vehicle to reduce greenhouse gas emissions and pollution, such as carbon dioxide (CO₂).³ As a renewable power source, batteries make the EV efficient and environmentally friendly.^{4,5} Different types of battery technologies have been proposed, such as lithium-ion batteries (LIBs), lead acid batteries, nickel-based batteries, and sodium-based batteries.⁶ However, with the worldwide electrification trend, LIB has become predominant in electronics, EVs, and energy storage stations, with superior properties of higher energy density and long lifespan.^{7–9} These industries call for better batteries with lower cost, fast charging rates, and enhanced subzero temperature performance/thermal stability in next-generation applications.^{10–12}

However, LIB performance is sensitive to certain factors in the operating environment, such as temperature,^{13,14} pressure,¹⁵ and vibration.¹⁶ The ambient temperature has a considerable influence on the overall performance of LIBs, such as capacity, available power, charging/discharging efficiency, safety, and lifespan. The temperature sensitivity of LIBs stems primarily from the temperature sensitivity of the physical and chemical properties of the material. LIBs exhibits higher efficiency and a longer lifetime under ideal operational temperatures.¹⁷ The thermal issue attracts attention to the precise battery thermal management system (BTMS) and current control to maintain the cell/module/pack temperature within the acceptable range (0–40°C). Considering the thermal safety and operational efficiency,^{18,19} the cell body temperature should be maintained within 15°C–35°C. The system temperature deviation should be controlled below 5°C to enhance the lifespan and operational performance.^{20–22}

BTMSs are proposed to satisfy these operating requirements, especially in extreme working conditions such as fast charging, severe high-temperature environments, or subzero cold zones.²³ Moreover, with higher requirements proposed for pure EVs, the energy density of LIB cells will be increased to extend the driving range. Fast charging technology will be widely employed to enhance long-term driving convenience.^{24,25} Therefore, battery thermal management is crucial for solving emerging problems in the all-temperature area EV industry,

such as severe lithium plating, overheating, and even thermal runaway (TR).^{26,27} Moreover, more research is needed to enhance thermal management efficiency, thermal uniformity, and energy cost to cope with the future harsh requirements of BTMSs. Most existing reviews are organized for pure thermal management methods or structures.^{28–30} This study provides a comprehensive overview and perspectives of LIB characteristics and thermal management strategies under all temperature areas and future requirements. As depicted in Figure 1, the basic idea behind this review is to give out the thermal performance, mechanisms, and strategies for the LIBs under all-temperature areas (1, low-temperature area [$<0^{\circ}\text{C}$]; 2, normal temperature area [0°C – 60°C]; 3 high-temperature area [$>60^{\circ}\text{C}$]), from the performance, mechanism, and thermal management strategies levels.

LOW-TEMPERATURE AREA

Performance level

Subzero temperatures result in a negative impact on LIBs: (1) lower charge/discharge ability,³¹ (2) less available energy and power capacity,³² and (3) shorter lifespan.^{23,33,34} The LIB output voltage decreases, causing lower energy density and power fading.³⁵ Consequently, the available energy loss under subzero temperatures reduces the EVs' driving mileages and available energy of the energy storage devices (ESDs). Moreover, the available power loss under subzero temperatures limits the quick acceleration and power frequency modulation of ESDs. Previous studies demonstrated that the 18650 LiPF₆ battery cell could only provide 5% and 1.25% of the power capacity (20°C) and energy capacity (20°C), respectively, under -40°C .³² The driving range of the 2012 Nissan LEAF was reported to drop significantly from 138 miles under the ideal operational condition to 63 miles under -10°C . The usable charge/discharge capacity was calculated under low-temperature constant current charging/discharging tests.^{32,36} Even in recent studies, with the development of battery technology, lithium-ion phosphate (LFP)/graphite-based battery cells could only provide available 70% and 60% capacities (refer to the room temperatures) under -10°C and -20°C , respectively. Furthermore, LIB rapidly degrade at subzero temperatures. You et al.³⁷ revealed that battery capacity fades nonlinearly after 500 cycles, under -5°C to 0.5°C cycling.

Under increasing charging rate requirements, lithium plating has more potential to occur, especially under a high state of charge (SOC) and subzero temperatures. Lithium plating facilitates gas generation, forming gas pockets on the electrodes, accelerating degradation, and even failure.³⁸

Mechanism level

Low temperatures cause LIB deterioration (decreased ionic diffusivity, electrolyte conductivity, and anode lithium-ion diffusivity). In addition, the lithium-ion intercalation capacity of graphite decreases.^{39,40} Moreover, the available capacity decreases with increasing internal resistance.^{5,41–43} The charging/discharging capacity and efficiency are worse than those in typical applications. Furthermore, lithium evolution may occur inside the battery cell during high-current charging, harming the charging efficiency, lifespan, and safety.

Similarly, suppose that the LIB operates at subzero temperatures. The activity of the active material inside a battery is considerably limited. In this case, the internal resistance and polarization voltage increase.⁴⁴ Furthermore, the charging/discharging power and capacity are inevitably reduced, causing irreversible degradation of the LIB capacity and buried safety hazards. During the charging process, under an electric field applied by the charging equipment, lithium ions are extracted from the cathode material into the electrolyte, move to the anode, and enter the anode material composed of graphite to form an LC compound. Lithium ions cannot enter the anode in a timely manner to form an LC compound

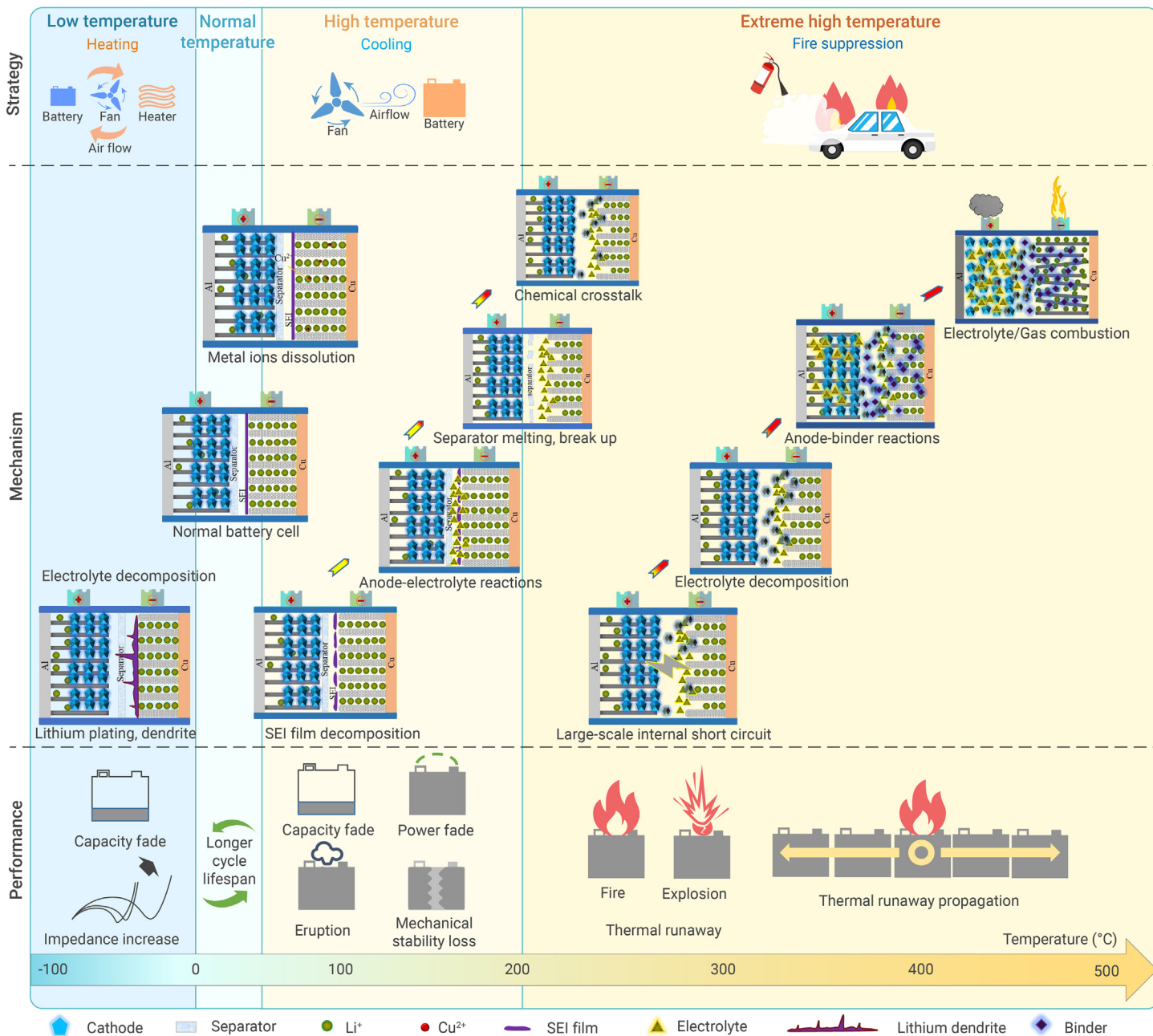


Figure 1. Performance, mechanism and strategies of lithium-ion batteries under an all-temperature area

while charging at high current rates and low temperatures. Lithium ions close to the negative electrode trap electrons, become metallic lithium, and aggregate to form lithium dendrites, which can grow. Piercing the diaphragm creates an internal short circuit.

Some existing research has proposed that the performance degradation of LIBs under subzero temperatures results from material property changes, which turns the stored energy into an unusable state.⁴⁵

As shown in Figure 2, the intrinsic low-temperature degradation mechanism includes the following aspects.

(1) Limited electrolyte conductivity and increased viscosity affect the Li-ion transport rate between the two electrodes. Moreover, it has been reported that inadequate electrode activity results in limited performance. Electrode activity implies the combined effect of marginalized Li-ion transport through the solid-electrolyte interphase (SEI) film, increased charge-transfer resistance, intrinsic loss of ionic conductivity, and slower lithium-ion diffusivity within the anode materials.^{46–48}

- (2) The chemical composition and physical characteristics of the SEI film are also critical, such as the resistance to lithium intercalation, which depends on the salt-forming electrolyte, anode material quality, SEI formation mode, and temperature.^{37,49,50} The SEI is the surface film on LIB electrodes, consisting of organic and inorganic components that maintain the electrolyte kinetically stable under an anode potential of less than 0.8 V. The SEI film thickness varies by approximately 0.5–80 nm, depending on the degree of anode graphitization.^{51–53} However, the anodic film is less permissible for lithium-ion transportation at the electrolyte/electrode interphase, significantly increasing the battery impedance.^{6,54,55}
- (3) The diffusion of solid-state lithium ions decreases significantly, especially during the charging process (lithiation),⁵⁶ which contributes to the polarization. The graphite anode was more likely to be affected by lithium plating during charging.
- (4) For the cathode material, the charge-transfer resistance increases by more than 200% compared with the normal charge-transfer resistance

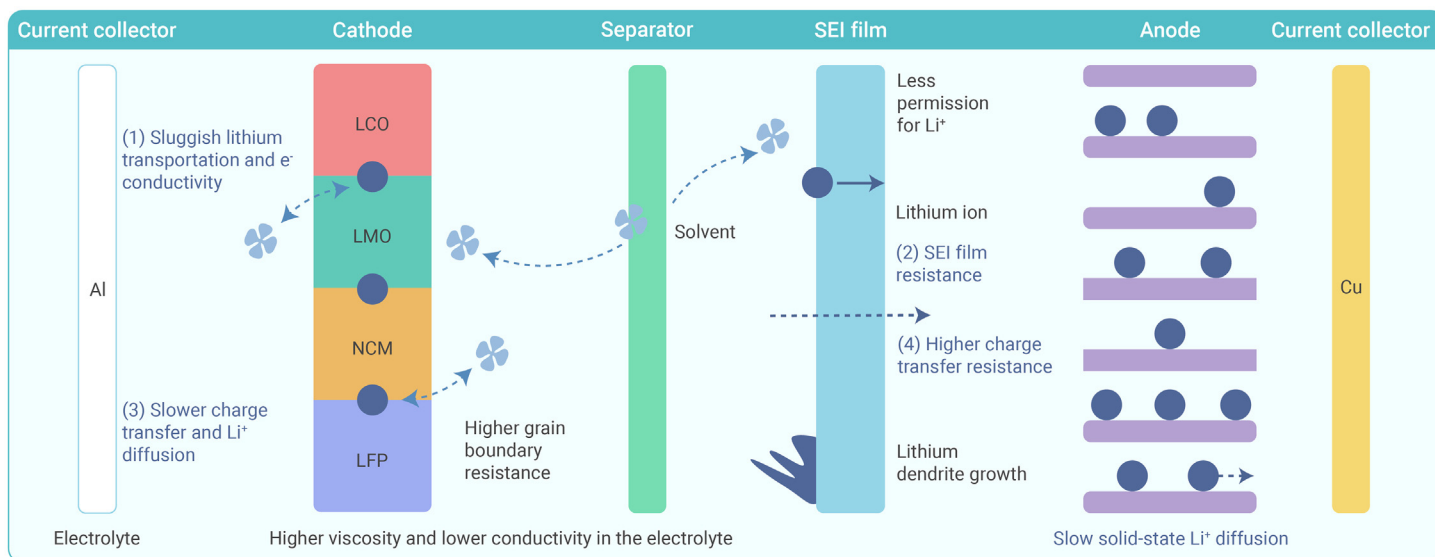


Figure 2. Battery degradation mechanisms under a subzero temperature area

during the discharging process (in the lithiated state).⁵⁷ Besides, high grain boundary resistance and slow solid-state diffusion contribute to the sluggish lithium transport and poor electronic conductivity of the cathode material.

Strategy level

Owing to the broad geographical applicability of automobiles, EVs inevitably operate in subzero temperature environments. Although a massive amount of heat is generated during the charging and discharging processes, the heat generated is insufficient for maintaining the cell within a suitable operating temperature range. Considering the limited charging and discharging performance in cold climates and high-altitude drone applications, preheating approaches are required to enhance battery performance at subzero temperatures.^{58,59}

Low-temperature performance enhancement strategies can be summarized at the material, cell, and system levels.

Material level

Cathode modification. Decreasing particle size. As depicted in Figures 3A and 4I, decreasing the particle size provides a shorter diffusion path length for lithium ions and electrons and a broader electrolyte/electrode surface area for lithium-ion insertion and extraction, which results in enhanced electrochemical kinetics and low-temperature performance.^{60,61} However, nanoparticles lead to more side reactions considering their high surface area and reactivity.⁶² In addition, many binders are needed to glue these small particles together, inevitably decreasing the capacity. The low-temperature performance of other cathode materials such as LiCoO_2 , LiMn_2O_4 , and V_2O_5 has also been enhanced by decreasing the particle size.⁶³

To avoid the nanoparticle electrode issues of reactive surfaces, limited particle contact, and retention of the merits of nanostructures, extensive studies have been conducted focusing on conductive coating materials and forming nanostructured electrodes.

Coating. As depicted in Figure 3B, similar to the carbon anode, electrolyte decomposition layers (EDL) still exist on the cathode surfaces.⁷¹ The electrochemical behavior on cathode surfaces depends on the EDL properties.^{72–74} Electrolyte component decomposition on the cathode is temperature sensitive⁷⁵ and depends on the electrolyte material.^{73,76} Commercial cathode components are LiF , Li_2CO_3 , ROCO_2M , ROCO_2Li , ROLi , MCO_3 , MF_2 (M = transition metal), and polycarbonates,⁷² respectively. Owing to its pronounced stability, EDL formation on the LiFePO_4 cathode differs from that on the Li_xMO_y host material (M = Ni, Mn).⁷⁷ Generally, the EDL thickness on LiFePO_4 is less than 5 nm in a 1 M LiPF_6 mixture of EC and DEC. An LiFePO_4 cathode

coated with a carbonaceous material prevents undesirable reactions and enhances EDL stability.^{78–81} Cathode coating significantly prevents contamination from HF and water.⁷² Compared with the pristine LiFePO_4 , a carbon-coated cathode capacity retention increases from 53.4% to 66.1% at -25°C .⁶⁴

As Figures 3B and 4II show, an appropriately thin carbon coating is beneficial for balancing sufficient conductivity and Li^+ penetration,⁸² especially for the superior electronic conductivity of carbon. Graphite is desirable for coating.^{83,84} Uniform carbon coating for LiFePO_4 particles provides access for electrons from all directions to achieve low polarization.⁸⁵ Organic carbon pyrolysis produces a more uniform carbon film,⁸⁶ and increasing the porous carbon film surface area improves the conductivity.⁸⁷ However, excessive carbon significantly decreases the tap density of LiFePO_4 and generates some by-products, such as Fe_2P .^{81,88} Therefore, the desirable carbon content in LiFePO_4/C is less than 5% wt.⁸⁹

3D conduction network. As demonstrated in Figures 3G and 4III, to further enhance the conductivity and electrochemical characteristics, a three-dimensional (3D) conduction network was proposed.⁹⁰ Chang et al.⁹¹ proposed a cathode material without any supplementary conduction agent. These results indicate that the prepared LiFePO_4 nanographite (platelet) heterostructure enhances electron transport. Wu et al.⁶⁴ proposed 3D carbon-decorated LiFePO_4 nanocomposites with ultrahigh rate capability and enhanced subzero-temperature performance. Kim et al.⁶⁵ proposed a catalyst-assisted self-assembly approach to embed graphene onto LiFePO_4 as the cathode material, which exhibited superior cycling performance and rate capability.

Novel cathode material. To enhance the cycling performance under low temperatures,⁹² as in Figure 4IV, Yoon et al.⁶⁶ investigated the subzero-temperature performance of $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ (NCM) cathodes with a 1.2 M EC-EMC (3:7 by volume) electrolyte. The results indicated that the low-temperature capacity of the NCM cathode was dependent on its chemical composition, which increased with increasing Ni content. Since high Ni content causes a high electrical conductivity, $\text{Li}[\text{Ni}_{0.85}\text{Co}_{0.075}\text{Mn}_{0.075}]\text{O}_2$ provides 127 mAh g^{-1} under a -20°C environment. Smart et al.⁹³ investigated the low-temperature performance of $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathode with a 1.2 M EC-EMC (20:80) electrolyte, which exhibited a 55% capacity retention at -40°C under high current rate discharging. The results indicated that a low ethylene carbonate content helped achieve a high discharge rate owing to its low viscosity and high ionic conductivity. Rui et al.⁹⁴ proved that an $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (LVP/C)-based battery material provided a high discharging capacity of 108.1 mAh g^{-1} under -20°C environment. Its low-temperature performance was enhanced by the low activation energy of LVP (6.57 kJ mol^{-1}), causing more access to Li^+ extraction/intercalation in LVP.

Electrolyte modification. More researchers have recently focused on enhancing the electrolyte stability with effective SEI film formation. These studies can be summarized as follows:

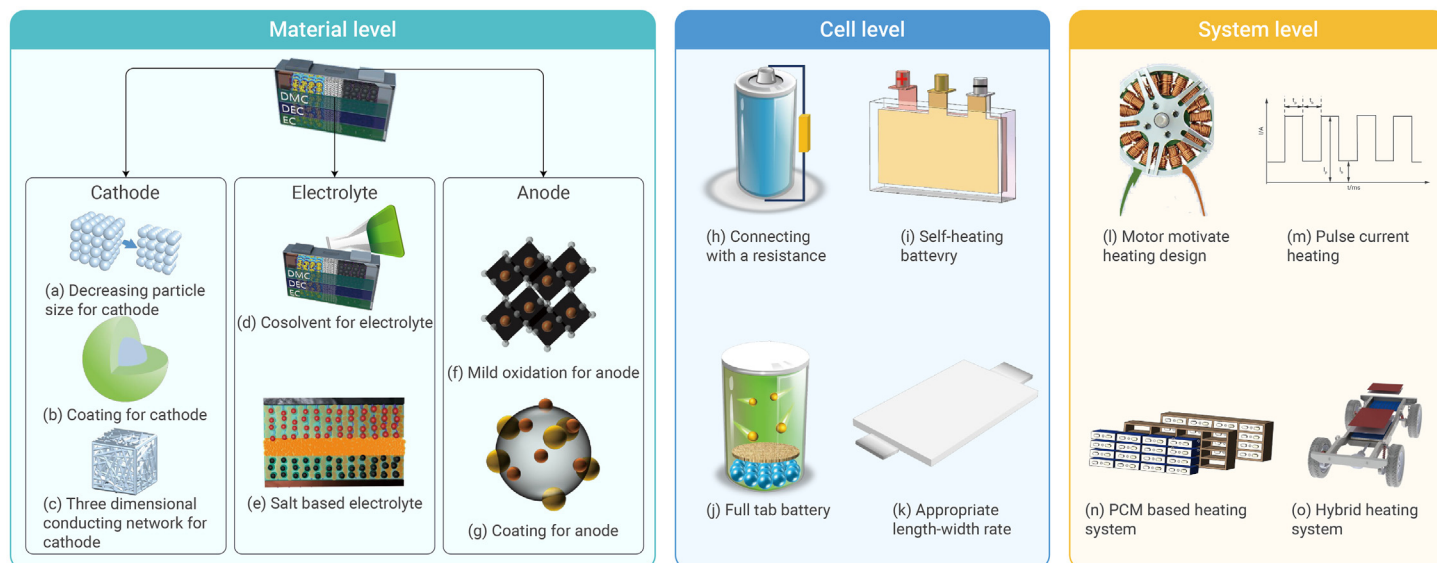


Figure 3. Strategies to enhance low-temperature performance of Li-ion batteries from different levels

- (1) utilization of cosolvents with lower viscosity and lower freezing temperature, such as glymes, esters, and lactones.^{95–98}
- (2) changing the lithium salt LiPF_6 with new mixtures improved the charge transfer resistance and other characteristics of the SEI film.^{99–104}
- (3) formulation of new electrolyte additives to lower the freezing temperature.^{105–109}
- (4) novel electrolyte design to maintain the ionic conductivity within a desirable range.¹¹⁰
- (5) LTO||LTO symmetric battery design to prevent high interface resistance owing to lithium-ion desolvation.^{111,112}

The electrolyte determines the ionic mobility and participates in the reaction of SEI film formation on the anode.¹¹³ The SEI film permits lithium-ion conduction, protects the electrodes, and prevents further electrolyte reduction, affecting the low-temperature performance and cyclic life.⁴⁷ Low-temperature performance can be achieved by improving the electrolyte conductivity and SEI stability at the electrolyte/electrode interface. The experimental results indicated that the electrolyte system can be optimized by adding suitable cosolvents and improving the Li salts.^{106,114,115}

Adding cosolvent. The electrolyte solution conductivity drops rapidly in a low-temperature environment owing to the high freezing temperatures of conventional solvents (EC, DMC).¹¹⁵ As depicted in Figure 3D, to reach a low freezing temperature but high conductivity under low temperatures, adding suitable cosolvents into the electrolyte has been proposed as a reliable method, which is selected considering some critical factors: (1) dielectric constant, (2) viscosity, (3) coordination behavior, (4) liquid range, and (5) pronounced chemical compatibility.

Salt selection. As Figures 3E and 4V demonstrate, Li salt selection also affects the lithium-ion conductivity and SEI stability, which is significant for enhancing the low-temperature performance.¹¹⁶ LiPF_6 is a commonly utilized Li salt. However, it spontaneously decomposes into LiF and PF_5 , thereby inducing structural changes and capacity fading. The selection of LiPF_6 with lithium tetrafluoroborate (LiBF_4) or lithium bis(oxalato)borate (LiBOB) enhances low-temperature performance because LiBF_4 or LiBOB -based electrolytes demonstrate low charge-transfer resistance.^{117–119}

Anode modification. Limited Li diffusion in the electrodes and higher charge-transfer resistance at high charge/discharge current rates result in higher polarization and limited performance.⁵³

The kinetic limitation of lithium-ion transfer at the electrode/electrolyte interface induces primary performance limitations at low temperatures. The electrochemical (faradic) reaction can be optimized by reducing R_{ct} and maintaining SEI stability.

Graphite is the most commonly used anode material for LIBs. However, its principal limitations are high R_{ct} values at the electrolyte-electrode interface,

SEI instability, and reduced solid-state lithium diffusivity. Effective methods for improving the anode include the discussion of the following.^{32,56,120}

Mild oxidation. As shown in Figures 3F and 4VI, mild oxidation of the graphite anode decreases the number of unsaturated carbon atoms at the edge planes, resulting in a smaller mean particle size.¹²¹ Furthermore, this approach causes the formation of nanovoids, nanochannels, and chemically bonded SEI.¹²² Consequently, the electrochemical impedance decreases, hindering the co-intercalation of solvated lithium ions and electrolyte decomposition. Mild oxidation can be achieved through thermal treatment or wet chemical oxidation.^{67,123,124}

Mixing. Mildly oxidized graphite mixed with metal nanoparticles demonstrates enhanced low-temperature performance.¹²⁵ As Figure 4VII depicts, the oxidized graphite anodes mixed with 1% Cu and Sn in a 1 M LiPF_6 EC-DEC-DMC (1:1:1) electrolyte were proved to have the capacities of 130 mAh g^{-1} ¹²² and 94 mAh g^{-1} ⁶⁸ at -30°C , respectively. The superior low-temperature performance resulted from the enhanced lithium-ion desolvation, increase in SEI conductivity, and internal conductivity of the metal-dispersed powder bulk electrode.⁶⁸

Coating. Anode coating has been proven an alternative method to enhance electrochemical performance.¹²⁶ As shown in Figures 3G and 4VIII, the oxidized graphite anodes coated with 50 Å Cu and Sn layers in a 1 M LiPF_6 EC-DEC-DMC (1:1:1) electrolyte was tested to have the capacity of 103 mAh g^{-1} ¹²³ and 152 mAh g^{-1} ⁶⁸ at -30°C , respectively. Gao et al.⁶⁹ prepared a Cu-coated graphitic carbon anode via plating. The stable SEI suppresses the electrolyte decomposition (1 M LiClO_4 PC-DMC, 1:1 by volume) and achieves promising LIB performance at -60°C .⁶⁹ Therefore, the metal layers on the anode cause a remarkable decrease in R_{ct} , a stable SEI, and an increased lithium conductivity.^{68,69,127}

$\text{Ag-Fe}_2\text{O}_3/\text{carbon}$ nanofibers (CNFs) anode materials demonstrated pronounced electrochemical performances at -5°C due to their synergistic effects on the CNF matrix and the conducting Ag.¹²⁸ Li et al.¹²⁹ proposed Fe/ Fe_3C -CNF materials with a high capacity of 250 mAh g^{-1} after 55 cycles at -5°C in a 1 M LiPF_6 EC-EMC-DMC (1:1:1 in volume) electrolyte.

Novel anode material. Raccichini et al.⁷⁰ synthesized a multi-layer graphene anode by combining microwave irradiation and ultrasonication in an ionic liquid. The low-temperature characteristics of multi-layer crystalline graphene (GRAL) and the commonly utilized graphite SLP30 in a 1 M LiClO_4 PC-DMC (1:1 by volume) electrolyte were compared. The results indicate that the GRAL capacity was higher than that of SLP30 at low temperatures. As shown in Figure 4IX, the low-temperature performance is enhanced owing to its high active surface area, which results in a higher anodic electrochemical reaction efficiency and improved lithium-ion diffusion kinetics.¹³⁰

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ is another promising low-temperature anode material with a high cycling stability. However, its sluggish lithium-ion and electron conductivities limit its electrochemical performance. Reducing the particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and coating are typical methods to enhance electrochemical performance.^{131,132} Yuan et al.¹³³ prepared nanosized rutile TiO_2 via a sol-gel approach, which

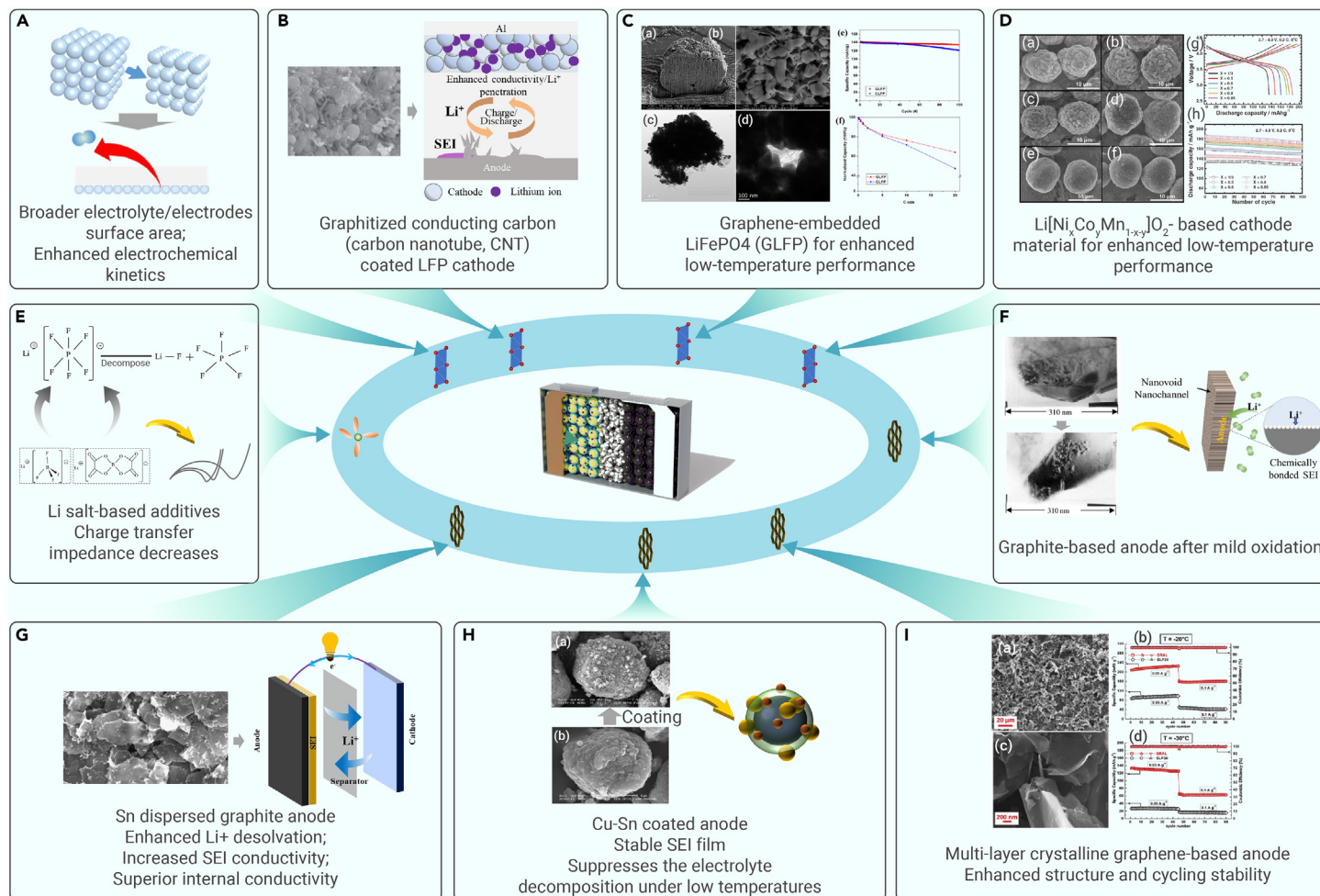


Figure 4. Schematic diagram of strategies to enhance low temperature performance (A) Decreasing cathode particles. (B) Coated cathode for enhanced low temperature performance (adapted from Wu et al.⁶⁴). (C) Graphene embedded LiFePO₄ (GLFP).⁶⁵ (D) Li[Ni_xCo_yMn_{1-x-y}]O₂-based cathode material.⁶⁶ (E) Li salt-based additives. (F) Mild oxidized anode (adapted from Wu et al.⁶⁷). (G) Mixed anode (adapted from Nobili et al.⁶⁸). (H) Coated anode (adapted from Gao et al.⁶⁹). (I) Multi-layer crystalline graphene-based anode.⁷⁰

provides a capacity of 77 mAh g⁻¹ at -40°C with a C/5 rate in a 1 M LiClO₄ PC-DMC (1:1 by volume) electrolyte.

Cell level

Connecting with a resistance. As depicted in Figure 3H, the battery cell can be connected to an external resistor, resulting in a closed loop. The current increased along the path inside the battery material. In addition, external resistance heats the battery surface. However, it is challenging to utilize and precisely control this heating approach in real applications, especially for massive battery cells in battery packs or energy storage stations, owing to local overheating and low heating efficiency.

Self-heating battery. As shown in Figure 3I, Wang et al.³⁹ proposed a self-heating battery cell by inserting an insulating polymer-coated metal foil. The switch between the activated and negative terminals can be closed to preheat the LIB to a low-temperature environment. Experimental results suggested that the battery temperature could be heated from -30°C to 0°C within 30 s through Ohmic heat generation. The switch was turned off until it reached 0°C, with 5.5% of the battery capacity consumed during the preheating process. Zhang et al.⁴⁰ concluded that nickel foil can accelerate spontaneous heat generation. There was a linear relationship between the inner temperature and the nickel foil resistance, which could be utilized as a temperature sensor to detect the internal temperature.

To enhance battery cell consistency, temperature gradients should be avoided.¹³⁴ However, a single nickel foil-based self-heating cell cannot ensure uniformity. Zhang et al.⁴⁰ proposed a self-heating cell with two or three pieces of nickel foil to address the issue. Moreover, the heating time was shortened, and the energy cost was reduced by 25%–30%. Compared with the slow heating

rate issue of some external heating approaches, the self-heating rate reached 1°C–2°C/s. However, internal resistance heating efficiency may be limited by the electrothermal conversion efficiency.⁵⁸ Furthermore, considering the internal short-circuit-based mechanism and the complex operational conditions of EVs, the safety issue of changing the Li-ion battery cell's inner structure should be paid more attention to.^{135,136}

Full tab battery. As demonstrated in Figure 3J, a full-tab battery has been proposed to achieve a trade-off between energy density and heat dissipation in recent years.¹³⁷ Conventional cylindrical batteries are commonly wound based on anode copper foil, cathode aluminum foil, and separator superposition. A pole lug was welded to both ends of the copper and aluminum foils for the outside electrode design. The winding length of a conventional 18650 cylindrical battery was 800 mm. To ensure low resistance, a long copper foil has high thickness and consistency requirements.

Taking the Tesla 4680 battery as an example, the full-tab battery converts the entire current collector into a tab, and the conductive path no longer depends on the tab. The current changes from the transverse transmission of the TS collector to the longitudinal transmission of the current collector. The entire conductive length decreased to 80 mm (battery height). The resistance is reduced from about 20 to 2 mΩ, calculated by the copper resistance formula. According to the ohmic heat theory, the internal resistance power cost can be reduced from 2 to 0.2 W.

Previous research has indicated that more tab numbers result in a less apparent internal temperature rise, and the current density of the battery tab increases, increasing the heat generation rate at the tab and causing a significant local temperature rise. The full-tab design effectively reduces the local current density and solves the thermal uniformity issue, which improves heat dissipation

and preheating efficiency. Therefore, the preheating efficiency, lifespan, and overall performance were enhanced when the batteries were heated using current.

Appropriate length-width rate for battery. As Figure 3K shows, large-scale battery cell schemes have been commonly used in recent years to achieve higher energy densities in battery systems. However, from the perspective of the current path, it is difficult to maintain thermal uniformity using a BTMS. In an inappropriate battery design, the current concentration around the tabs is different, which induces different heat accumulation issues, significantly affects the thermal uniformity and preheating rate, and can even cause overheating. In addition, a large cross-sectional area results in insufficient preheating efficiency. Therefore, an appropriate length-width ratio is important for battery design, especially in cold areas.

System level

As shown in Table S1, the preheating strategies utilized at the system level were evaluated and compared from various perspectives (heating rate, thermal consistency, safety, cost, and applicability).

Air heating. The air heating system flows hot air through the battery system.^{22,138} The battery cells can be warmed by heat exchange between the airflow and battery surfaces.¹⁸ Figure 5H shows that the air-cooling structure is designed based on air convection combined with heaters and control elements. Song et al.¹³⁹ found that the cell capacity was enhanced by 3.1% under a -3°C environment with a 5 kW heater-based air heating structure. Zhang et al.¹⁴⁰ utilized the EV's air conditioning system combined with pentadecane ($\text{C}_{15}\text{H}_{31}$) as the heat transfer medium under an ambient temperature lower than 0°C . The results demonstrated that the preheating efficiency, based on the phase change of pentadecane, was higher than that of the refrigerant. This strategy can be combined with an air-cooling system by combining the BTMS with heater control.

Liquid heating. Liquid heating is an approach for heating the cooling liquid to a specific temperature through the heating components of the vehicle, and the bump can be utilized for cycling the heated coolant in the battery module/pack.¹⁴¹ To achieve all climate applications with low volume and weight costs, the liquid heating loop is commonly incorporated in the liquid cooling system. As shown in Figure 5F, a direct liquid heating system is proposed based on nonconductive transformer oil, a heating film, and a heat insulation layer. Nelson et al.¹⁴² concluded that a silicone-oil-based liquid preheating system is effective for the cold start of LIBs. Wang et al.¹⁴³ inserted an L-shaped heating plate into the cell gap, and the fluid temperature of the heating plate evaporator was set to 40°C . Simulation results indicated that the preheating time of the battery module from -20°C to 0°C was controlled within 500 s.

PCM heating. Phase-change materials (PCMs) have received extensive attention owing to their latent heat without an extra power supply, which is a typical active heating/cooling approach.¹⁴⁴ As demonstrated in Figure 5E, latent heat can also be utilized for preheating under subzero temperatures. Zhong et al.¹⁴⁵ proposed a PCM-resistant wire-based BTMS with a fin for -20°C application. The central part's temperature of the battery module can be increased by 40°C within 300 s. Moreover, the fin structure can be utilized to prevent the thermal saturation prevention. Ling et al.¹⁴⁶ compared the heating effects of various composite PCMs. However, the proposed PCM did not have sufficient thermal conductivity, which resulted in a severe temperature deviation, uneven voltage distribution, and capacity loss. Therefore, to fulfill the requirements of fast charging and all-climate applications in next-generation BTMSs, PCM cannot achieve the desired thermal conductivity, volume, weight, latent heat density, and price.

PTC coupled heating. Positive temperature coefficient (PTC) resistance is a typical external heater based on the principle of Joule heat generation.¹⁴⁷ The metal heating wire is generally encapsulated in an insulating layer.¹⁴⁸ Li and Huang¹⁴⁹ proposed an aluminum plate scheme twinned with a PTC resistance wire for battery preheating. Fan et al.¹⁵⁰ conducted a simulation study to analyze the influential factors of a heating-plate-based BTMS. The results indicated that the heating efficiency increased with the coolant flow rate and coolant temperature. However, the maximum temperature exceeded 40°C when the inlet temperature was above 50°C . Chen et al.³³ conducted a thermal analysis to compare the preheating efficiency of two PTC-liquid heating systems under a -40°C environment. It was demonstrated that the preheating speed, thermal uniformity, and power consumption could be

enhanced through appropriate structural design and preheating interval settings.

Alternating current heating. The feasibility of alternating current (AC) preheating in battery systems has been verified by setting alternative pulse currents through batteries.^{151,152} Joule heat can be generated for preheating. Previous experimental results indicated that a high current amplitude was beneficial for temperature uniformity, and that the LIB performance did not degrade significantly.¹⁵³

Zhang et al.¹⁵⁴ developed a sinusoidal AC heating structure with thermal insulation design. Repeated experimental results indicated that the preheating speed was positively correlated with the amplitude and heat insulation and was proven to have a negative correlation with frequency. Moreover, no significant capacity loss was observed after the tests. Furthermore, a lumped energy conservation model was proposed to predict the temperature rise for real-time preheating control.¹³⁴ Zhao et al.¹⁵⁵ compared the preheating efficiency of pulse heating and constant-current/voltage charging and found that the charging time could be shortened by 36 min (23.4%) and the charging capacity could be increased by 7.1% with pulse heating under the same operational conditions.

Ruan et al.¹⁵⁶ proposed an electrothermal coupling model-based internal heating system. A constant polarization voltage was controlled during heating to achieve a trade-off between the preheating interval and minor capacity loss. The heating efficiency of variable-frequency preheating was found to be consistent with that of constant-frequency heating. Therefore, constant-frequency heating can be selected for real applications, considering the feasibility of variable-frequency preheating.

A DC-DC converter can be used to amplify the output voltage to reach the desired charging voltage. Although external heating elements are not required for mutual pulse heating, their unique circuit and control elements increase the cost of the preheating system.¹⁵⁷

Heating preservation. In summer, external high temperatures increase the LIB temperature. However, in severely low temperatures or winter, the internal temperature of the LIBs drops rapidly after parking outside for a long time, which affects the recharging, starting, and speed performance of the EV. Therefore, it is necessary to eliminate the impact of external high temperatures in summer or low temperatures in winter on the battery system through a thermal insulation design.¹⁵⁸ Insulation materials are employed to insulate and reduce the impact of external environmental factors.

A heat preservation system is commonly integrated with a BTMS to enhance cooling/heating efficiency, and energy consumption can also be controlled.

NORMAL TEMPERATURE AREA

Performance level

Ambient temperature directly affects the activity and conductivity of the electrode material, the insertion and deintercalation of lithium ions on the electrode, and the lithium-ion permeability of the separator. Furthermore, ambient and internal temperatures affect the electrochemical reactions inside the battery cell. Therefore, LIBs have a normal operating temperature range without severe heat generation.

As the temperature increases within this range, the activity of the internal active materials is enhanced, and the charging/discharging voltage, efficiency, and capacity of the battery increase accordingly, resulting in a corresponding reduction in the internal resistance. However, as Figure 6 depicts, the internal side reactions accelerated when the battery temperature exceeded a specific range. These side reactions consume lithium ions, solvents, and electrolytes, degrading the battery performance. Previous studies demonstrated that LIB cycle life is significantly reduced when the battery works above 60°C . This phenomenon is more evident during high-rate charging and discharging, and can lead to accidents.

The calendar lifespan of EVs and hybrid electric vehicles was defined as 10 or 15 years.¹⁵⁹ However, the LIB temperature can be easily elevated to a relatively higher value, such as 40°C , which accelerates the ageing process, resulting in the loss of the retention capacity.

LIB performance is also influenced by temperature rise and deviation resulting from heat generation, ambient temperature, and different degrees of electrochemical reactions that occur at all times.

Existing studies have proven that the heat-generating rate of LIBs has a quadratic relationship with the charging/discharging current. At high

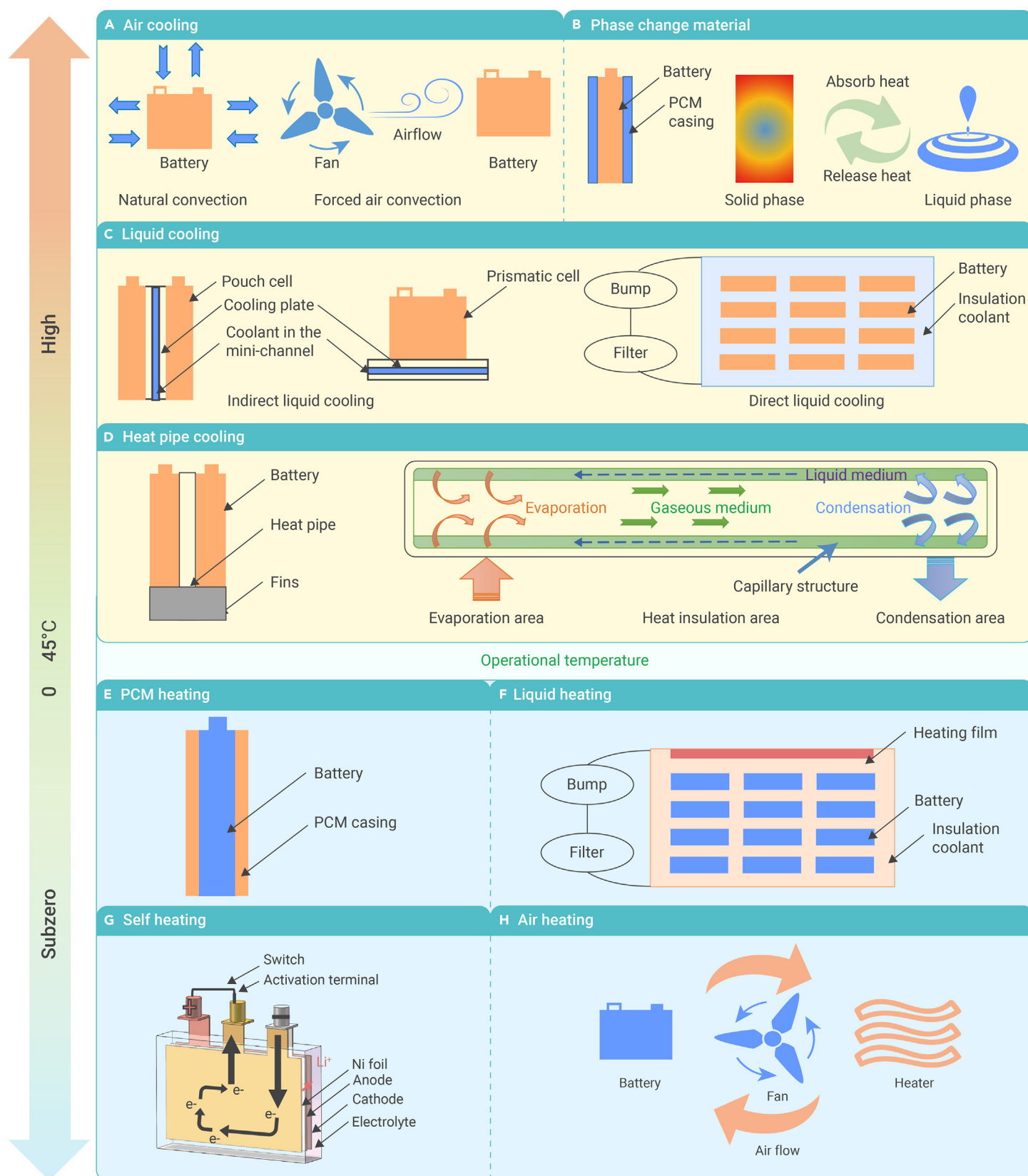


Figure 5. Scheme of thermal management strategies (A) Air cooling, (B) liquid cooling, (C) phase change material cooling, (D) heat pipe cooling, (E) PCM heating, (F) self-heating battery, (G) liquid heating, and (H) air heating.

ambient temperatures or during high-rate charging/discharging, the corresponding heat dissipation methods should be utilized to control the increasing temperature. Otherwise the cell will be overheated, causing performance degradation, a shortened lifespan, or even a dangerous state of TR.

Mechanism level

Almost all main/side reactions are related to temperature. The side reaction rate increases at high temperatures. Moreover, self-heating and thermal accidents can occur when the temperature exceeds a certain threshold. At subzero temperatures, the polarization increases owing to the increase in internal

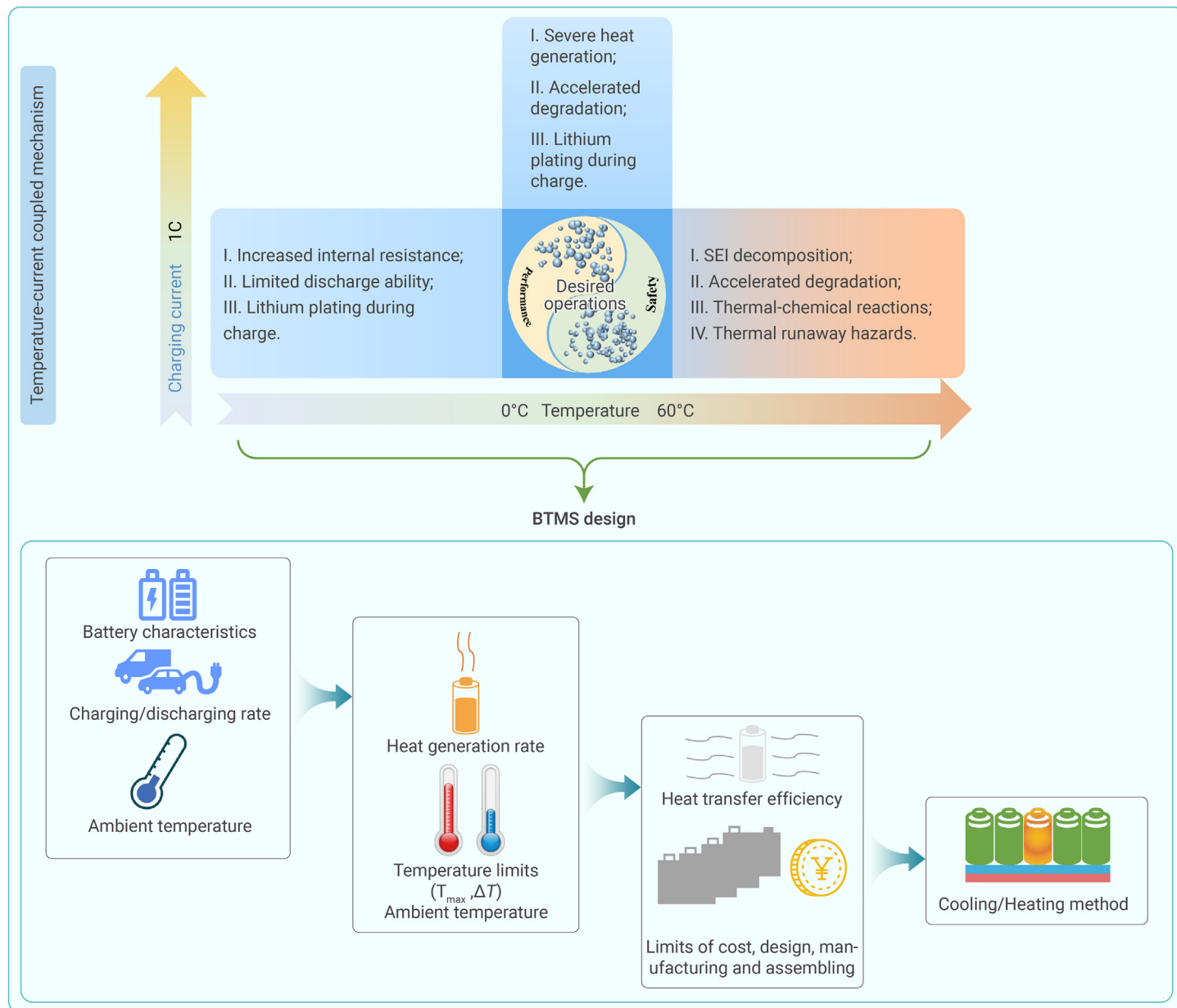


Figure 6. Schematic diagram of the temperature-current coupled mechanism and BTMS design for lithium-ion batteries

resistance, causing other side reactions. Charging at low temperatures triggers lithium deposition, accelerates degradation, and causes safety issues. Furthermore, material embrittlement under subzero temperatures limits battery cycle life. Therefore, maintaining battery temperature within the above-mentioned temperature range (15°C–35°C) is significant for the overall performance and cycle life.

In the normal temperature range, batteries exhibit desirable operational efficiency. The lithium ions were smoothly inserted and extracted from the anode. Only the degradation (loss of active material/lithium inventory/conductivity) and heat generation mechanisms during the cycling process affect the battery thermal performance, rather than the other side reactions.¹⁶⁰ The heat generation mechanism under the normal temperature range is discussed in the [supplemental information](#).

Strategy level

Under normal temperature conditions, LIBs do not require heat or fire suppression. However, heat generation during conventional charging/discharging cannot be neglected because it may exceed the threshold of some side reactions. The cooling component of the BTMS is used to prevent overheating. Because of the

characteristics of the battery system, thermal consistency should be maintained to guarantee the desired performance and cycle life of the battery system.¹⁶¹

According to the heat transfer media, the commonly used cooling methods in the EV market can be divided into three main categories (1) air cooling,¹⁶² (2) liquid cooling,¹⁶³ and (3) PCM cooling.¹⁶⁴ In addition to being distinguished based on the cooling medium, cooling is often classified as active or passive based on whether additional energy is consumed in the cooling process. Cooling efficiency is mainly characterized by the convective heat transfer coefficient. Generally, the convective heat transfer coefficient required by the BTMS is determined by the operational environment of the EV, LIB characteristics, and other factors, such as weight, volume, and cost.

As shown in [Figure 6](#), the selection of cooling approaches included the following steps: (1) confirmation of cooling system objectives, (2) calculation of heat generation power, (3) establishment of a battery model, (4) thermal fluid dynamic simulation analysis, (5) convection coefficient analysis, and (6) cooling method selection.

[Table S2](#) summarizes the critical technical standards for the typical cooling strategies for battery systems. A detailed discussion of the specific cooling approaches is provided in the [supplemental information](#).

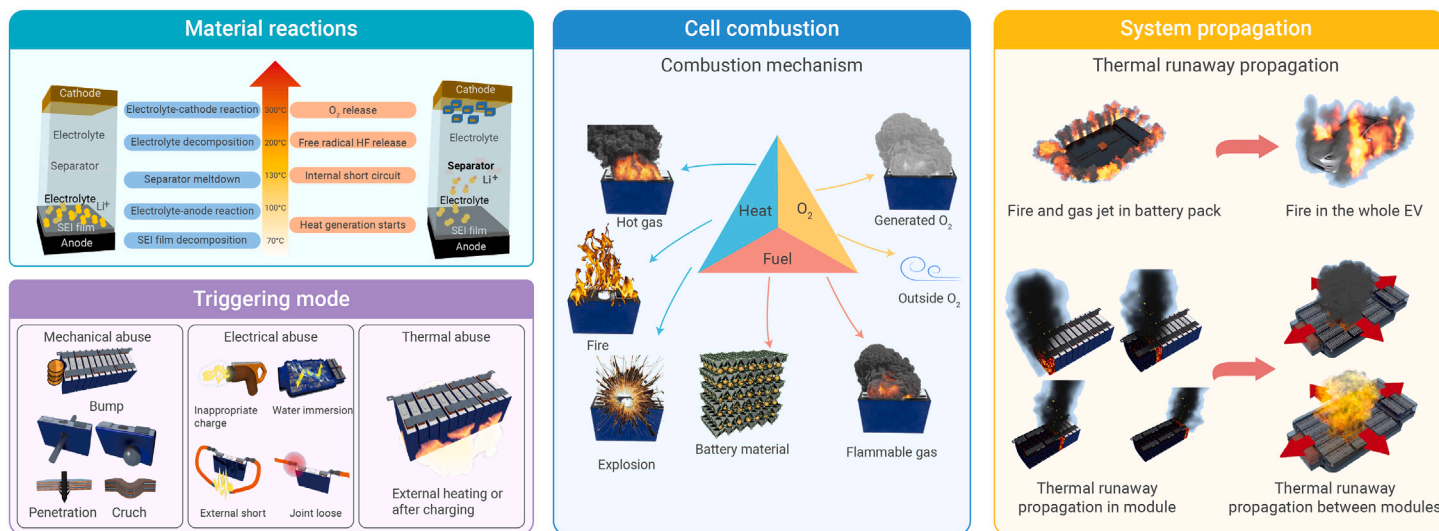


Figure 7. Thermal runaway scheme of lithium-ion under extreme high temperatures (Triggering mode; Mechanism; Fire resources; Thermal runaway propagation paths).

HIGH-TEMPERATURE AREA

Performance level

Fire behavior. As demonstrated in Figure 1, when the battery temperature exceeds 60°C, high temperature triggers SEI film decomposition and self-heating. Massive heat is released under high-temperature areas or abuse operations owing to chemical reactions and ISC, and the battery temperature rises rapidly.¹⁶⁵ Simultaneously, the safety valve opens when the internal pressure reaches a threshold, or the battery casing swells and breaks. Furthermore, aerosols and flammable gases are ejected at high speeds and temperatures.¹⁶⁶ These flammable materials tend to ignite in air when the air-fuel mixture ratio is within the flammability range, resulting in combustion.¹⁶⁷

Ping et al.¹⁶⁸ carried out a full-scale burning test for a 50 Ah LFP/graphite battery pack. The combustion behavior of a 100% SOC pack can be divided into several stages: (1) battery expansion, (2) jet flame, (3) stable combustion, (4) second flame jet, (5) stable combustion, (6) third flame jet, (7) stable combustion, and (8) abatement and extinguishment.

Thermal runaway propagation. An increasing number of battery cells are tightly connected in series or parallel to meet the demand for capacity and power in EV battery packs and energy storage stations.¹⁶⁹ As in the Tesla Model S, the battery pack is equipped with seven thousand 18650-format LIBs, and the total energy reaches 85 kWh. However, the total heat released from the battery module is not the sum of the combustion energies of each cell. The proportion is proven to be 1.26.¹⁷⁰ Therefore, TR and fire may propagate throughout the module/pack. A TR fire promotes the combustion of other cells to a higher fire intensity, resulting in catastrophic disaster.¹⁷¹

Generally, the thermal runaway propagation (TRP) from the center cell through the entire pack is faster than TR initiation from the corner.¹⁷² In addition, the electrical connection mode influences the TRP characteristics within a battery module.¹⁷³ Ten 18650-format cylindrical LIBs were connected as an equilateral triangle module, and the center cell was penetrated to trigger TRP. The results indicated that the parallel configuration resulted in an external short circuit with other cells. The surrounding cells were triggered in the parallel-connection mode rather than in the series-connection mode.

The battery format (cylindrical/prismatic/pouch) also affects the TR dynamics. Owing to the limited physical contact between neighboring cylindrical battery cells, the cylindrical battery module was less prone to TRP than the pouch cell module.^{173–175} Heat transfer between neighboring pouch cells was identified as the primary driving force for TRP.¹⁷⁶

There are three heat transfer paths within the battery module during the TRP process: (1) heat conduction through the battery shells, (2) heat conduction through the pole connectors, and (3) convection and radiation from the flame to the battery cells. Feng et al.¹⁷⁷ concluded that heat was mainly transferred through the shell, which mainly depended on the TRP behavior, and was approximately ten times higher than the heat transfer through the pole connectors. The

heat that triggers the neighboring cell for TRP is less than 12% of the total heat released during the TR process. The thermal resistance between the neighboring cells and the triggering methods determine the TRP characteristics within a battery module.^{177–179} However, flame impingement determines the fire propagation within a battery module. The flame and convection/radiation from the flame significantly affect the temperature of the LIB in contact.¹⁸⁰

Mechanism level

The self-heat generation of LIBs occurs in high-temperature environments or under electrical/mechanical abuse. When the accumulated heat from the exothermic reactions cannot be dissipated into the environment, the battery temperature increases continually. Furthermore, the impervious SEI film breaks down and dissolves, exposing the anode surface to electrolytic corrosion accompanied by irreversible lithium loss. Moreover, SEI film dissolution disturbs the physical balance state of the SEI metastable organic components, which form a more stable inorganic material such as lithium carbonate.¹⁸¹ The ionic conductivity and permeability of the SEI film gradually decrease as the inorganic carbonate ratio increases, causing a significant reduction in the LIB energy capacity and output power.^{182,183}

As shown schematically in Figure 7, the meltdown process of the cell consisted of three steps. The first step is the electrochemical breakdown of the anode SEI film, which starts at around 70°C.^{184–186} Besides, the intercalated lithium reacts with $(\text{CH}_2\text{OCO}_2\text{Li})_2$. When the heat is insufficiently dissipated from the LIB during this step, the governing electrochemical reaction becomes self-sustained.

Without protection from the SEI film, the following reaction is between the electrolyte and carbon anode.¹⁸⁷ Furthermore, if the self-heat generation rate exceeds 0.2 °C/min, the defined TR phenomenon occurs.^{188,189} The melting temperatures of the PE, PP, and ceramic-coated separators are around 135°C, 166°C, and 200°C, respectively.¹⁹⁰ The second step of the separator meltdown process commonly starts at around 130°C, with the symbol of exothermic activity on the cathode. In this step, the self-heat generation rate of the cell increased to approximately 5°C/min. The cathode and anode layers are in direct contact with each other, resulting in a large-scale internal short circuit,¹⁹¹ which is a critical inducement of TR. The energy released during the TR process is approximately equal to the energy stored in the battery cell.¹⁹² However, LIB TR can also be triggered without ISC, and may be induced by chemical crosstalk.¹⁹³

The final step began at temperatures greater than 200°C. Oxygen is rapidly released during the cathode decomposition,¹⁹³ and the self-heat generating rate of the cell increases to higher than 10°C/min with the decomposition of the cathode, the oxidation/decomposition of the electrolyte. The temperature increases to 100°C/min in some severe meltdown processes,^{184,194–196} releasing carbon dioxide, fluoride gas, and hydrocarbons.^{197–200}

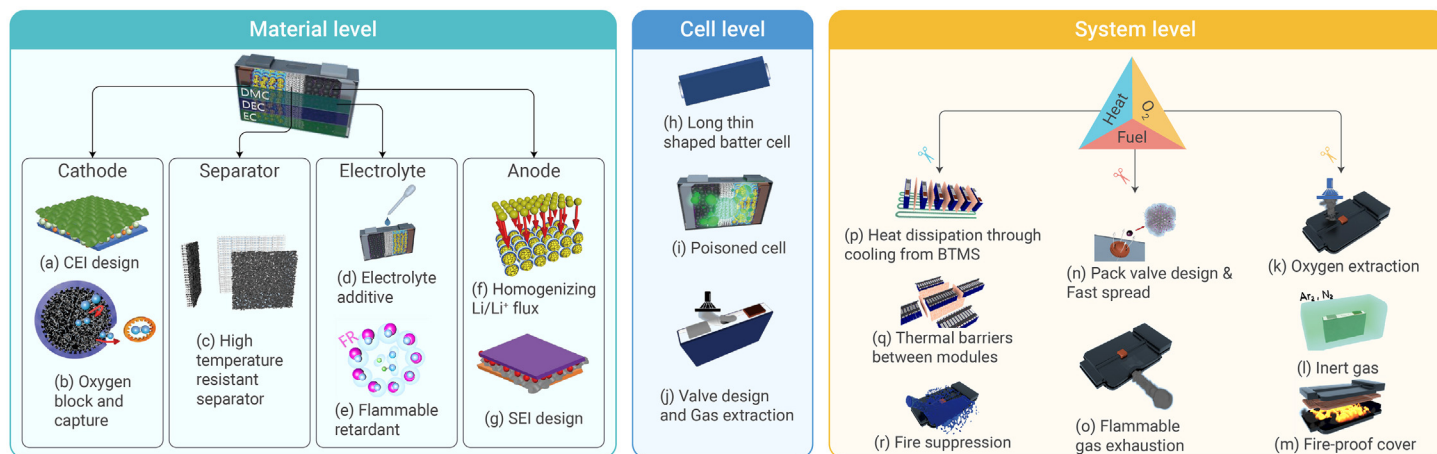


Figure 8. Thermal runaway mitigation strategies for Li-ion batteries from different levels²⁰⁵

The driving temperature for the exothermic TR reaction depends on the chemical components and the SOC.^{201,202} Generally speaking, with a higher voltage or SOC value, the onset temperature for the LIBs, TR is lower. However, even for specific battery types with the same chemical components, the onset temperature varies with load history and abuse events.^{184,203}

Strategy level

As summarized in the previous analysis, heat and flammable gas generation directly determine the TR hazard. Therefore, battery system safety can be enhanced through the following approaches: (1) preventing or alleviating heat and gas generation and (2) managing heat and gas generation. Safer battery cells can be fabricated by modifying the materials, inner structures, or safety devices. The incorporated safety equipment can be classified as a safety vent, current interrupt device, shutdown separator, detection component, BMS, BTMS, or fire suppression device.^{204–206} Furthermore, from a thermal management perspective, battery system safety can be enhanced by equipping an efficient BTMS and fire suppression devices.

Material level

Based on a previous study on the TR mechanism, the quantified TR mitigation target was to increase the self-heat generation temperature (T1) and TR onset temperature (T2) to inhibit TR triggering and to decrease the maximum temperature (T3), which decreases the heat released during the TR process.²⁰⁵

Cathode modification. Oxygen block and capture. In addition to the flammable gases generated during the TR process, oxygen released from the cathode has been proven to be a significant TR factor, resulting from the cathode-anode chemical crosstalk.¹⁹³ Therefore, as demonstrated in Figure 8B, a cathode coating is proposed as an intuitive method to block the release pathway for O₂.^{207,208} However, a specific solution is needed for the cathode coating to immediately capture the active O₂ release with reliable electrical performance and cycle life. Feng et al.²⁰⁵ proposed replacing the polycrystalline secondary structure with a single-crystal morphology to reduce the O₂ release surface area.

Separator modification. As depicted in Figures 8C and 9I, to postpone the occurrence of large-scale ISC, a high-temperature resistance separator should be designed against shrinkage in a hot environment,²⁰⁹ such as by selecting a thermal-resistant base material and coating with ceramic or other materials that do not break up under high temperatures. Rahman et al.²¹⁰ prepared a separator coated with boron nitride nanotubes. Results indicated that the proposed separator enhances the thermal stability up to 150°C without blocking the lithium-ion diffusion.

Anode modification. The coated layer on the anode surface also remained intact during cycling, preventing lithium metal deposition on the anode-electrolyte interphase. Therefore, there is no massive irreversible lithium plating on the anode to induce large-scale ISC. As depicted in Figure 9II, Friesen et al.²¹² prepared an anode material coated with Al₂O₃, which suppressed Li dendrite growth and demonstrated no deterioration in the thermal and mechanical safety behavior, despite thick Li deposition on the anode surface.

Electrolyte modification. Electrolyte selection. As Figure 8D shows, a more stable SEI film formation is required to postpone the self-heat generation state, which can be achieved by adding electrolyte additives.²¹⁴ Ma et al.²¹⁵ investigated the impact of electrolyte additives (vinylene carbonate [VC], fluoroethylene carbonate, and vinyl ethylene carbonate) on electrode/electrolyte reactions. Results indicated that adding VC decreases the lithiated graphite-electrolyte reactivity below about 200°C. Liu et al.²¹⁶ proved that electrolyte additives enhance SEI uniformity and suppress dendrite growth.

As depicted in Figures 8E and 9III, flame-retardant electrolyte additives have also been considered as alternative mitigation approaches in recent years. Hou et al.²¹⁷ proved that flame-retardant fluorinated electrolytes reduce heat release during the TR process, which guides safer LIB design through appropriate electrolyte design.

Cathode-electrolyte interphase design. To pursue higher energy density, the nickel content in the cathode material has been increased in recent years.²¹⁸ As Figures 8A and 9IV demonstrate, *in situ* robust cathode-electrolyte interphase formation and control are considered the promising cathode enhancement strategy to address the aggressive thermal reaction by forming a protective layer on the cathode, which has been investigated through appropriate electrolyte selection (conventional carbonate-based electrolyte, fluorinated electrolyte, concentrated electrolytes, or solid-state electrolyte) and adding additives.²¹¹ Besides, the operational environment, such as temperature and pressure, should be precisely controlled during pristine and post-cycling to achieve a stable and uniform interphase formation.

Cell level

Blade battery cell. As shown in Figure 8H, a blade battery cell is proposed with a trend of higher system energy density and larger scale. Zhang et al.²¹⁹ observed the TR front phenomenon in a long-shaped battery, which propagated at a moving rate. In real applications, an ISC failure after lithium planting or a defect inside it generally triggers TR accidents. A severe TRP temperature increase within a cell or battery system can be detected by a BMS and stopped by fire-distinguishing devices. In addition, thin, long battery cells were designed with fewer electrode layers. The energy released from the ISC is less than that from conventional batteries, especially when the LIB is penetrated/squeezed/triggered by a defeat ISC/partially overheated. The heat that propagates to other areas or neighboring cells is less and can even be cooled with proper heat dissipation or other mitigation countermeasures. Therefore, a long battery design is beneficial for TRP mitigation.

Self-poisoned battery cell. As Figure 8I shows, to reduce the heat released during the TR process, neutralizing the oxidant and reductant is considered a promising strategy for mild reactions,²²⁰ which can be achieved using the following methods.

- (1) application of thermoresponsive materials to block the cathode-anode contact.^{221,222}
- (2) structural design of current collector to isolate damaged area.²²³

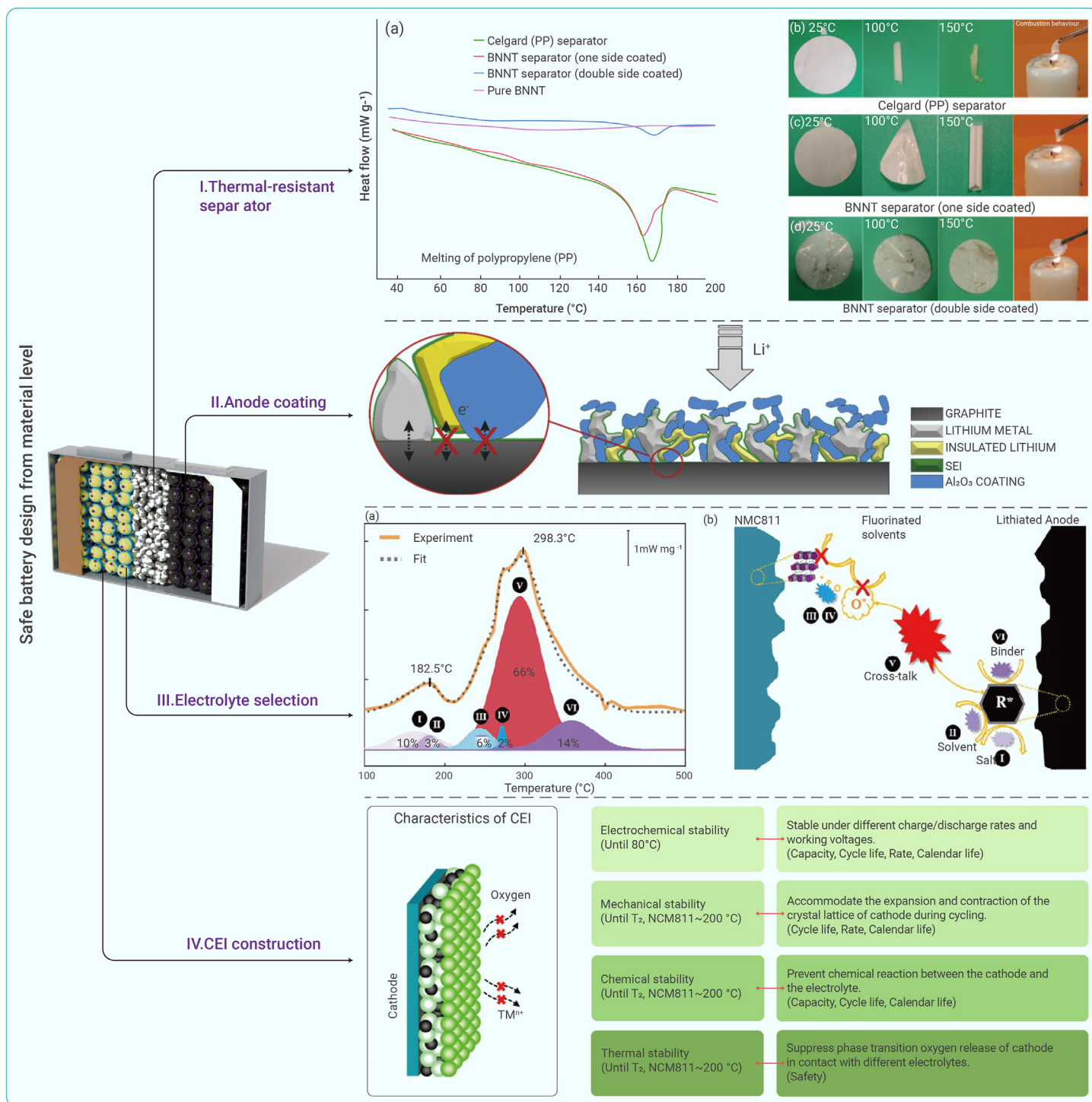


Figure 9. Schematic diagram of safe battery material design (I) Cathode-electrolyte interphase [CEI] design.²¹¹ (II) Thermal-resistant separator.²¹⁰ (III) Al_2O_3 -coated anode,²¹² and (IV) flame-retardant electrolyte.²¹³

Liu et al.²²⁴ prepared an electrospun separator with a core-shell structure containing a flame-retardant liquid within the microfibers. Lai et al.²²⁵ utilized a poison agent to mitigate the TR process, and results indicated that the energy release was significantly reduced and the maximum temperature was decreased by more than 300 $^{\circ}\text{C}$. However, it is necessary to guarantee the normal operation of LIBs. A reliable packaging material is urgently needed for the poisoning material to prevent the long-term corrosive effect from the electrolyte, the suppression behavior due to the LIB "breathing effect." In addition, avoiding internal structural changes in ISC is critical for safety during long-term cycling.

Safety valve design and gas extraction. As depicted in Figure 8J, proper design of the battery vent valve is significant for controlling the rupture moment

at an appropriate temperature level, which might help diminish the venting damage and TRP.²²⁶

System level

Detection devices. To avoid abnormal temperature environments or electrical loads, a BMS can be incorporated with a battery system for battery state monitoring.²²⁷ With timely detection and reporting of abnormal battery states, it is helpful to avoid overheating,²²⁸ overcharging, or overdischarging.²²⁹ In addition, BMSs utilize effective methods (such as timely discharge) to alleviate abuse conditions, even preventing TRP disasters.²³⁰ However, it is challenging for BMSs to detect ISC, which results from various factors, including manufacturing.¹⁷⁹

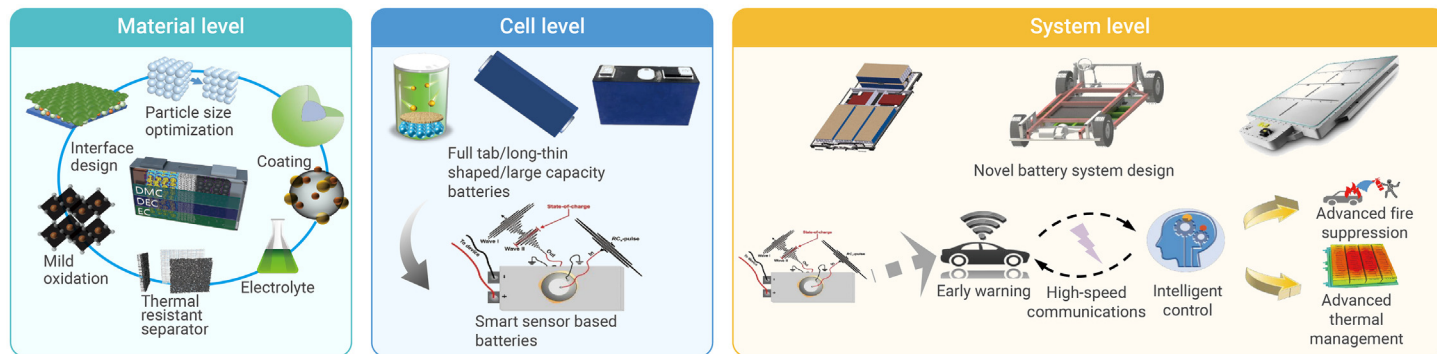


Figure 10. Future strategies to enhance the all-temperature area performance and safety

Apart from the temperature, current, and voltage detection of LIBs,²³⁰ gas and smoke detection²³¹ during the TRP process is also significant, especially within a battery system with a progressively larger size and higher energy density.²³²

TR propagation mitigation design for oxygen. Oxygen extraction. As shown in Figure 8K, oxygen extraction using a mini-bump may be helpful for TR fire mitigation, even if oxygen is generated from the cathode during the TR process. Continuous gas extraction cannot provide sufficient oxygen for the flame reaction, and TR propagation may stop.

Inertia gas environment. As Figure 8L demonstrates, wrapping the battery system in an inert gas environment helps suppress the TR fire propagation.^{233,234} Diluting the flammable gases and oxygen to a lean level might eliminate the flame.

Fire-proof cover. As shown in Figure 8M, attaching a thick fireproof cover on top of the battery system prevents fire from spreading. In addition, when a fireproof cover is designed with reliable sealing ability, oxygen can be decreased to a certain level with continuous consumption during the flame reaction. Furthermore, to protect passengers, a fireproof cover is essential to insulate the battery system from the cabins.

TR propagation mitigation design for fuel. Pack valve design and fast spread. As depicted in Figure 8N, when the pressure resistivity of the pack vent valve is lower than that of the pack wrap, expected venting occurs, and gases emerge from the vent valve. The gases can vent spontaneously once the pressure requirements are satisfied.

Flammable gas exhausting. As shown in Figure 8O, the gases inside the battery system can be extracted from the pack by using a bump with an appropriate gas channel design. Therefore, without sufficient flammable gases and oxygen, the TR fire cannot spread to the LIB even if the first cell is fired during the TR process.

TR propagation mitigation design for heat. Cooling. As Figure 8P shows, the heat conduction and dissipation efficiency of the commonly utilized liquid cooling system can be reinforced to prevent TR propagation.²⁰⁶ Moreover, PCM barriers can be combined to absorb the massive heat during the TR process.²⁷ To cope with the dilemma of high energy density and thermal safety, higher heat capacity and composite PCM barriers are considered promising solutions for TR propagation prevention in high-nickel ternary material battery systems.

Heat insulation. The heat transfer pathway through the surfaces between adjacent cells is the primary heat source, as shown in Figure 8Q. Setting thermal insulation barriers between neighboring cells and battery modules is a cost-effective method for mitigating TRP.

The proposed heat-insulation materials include ceramic plates, rock wool panels, glass fibers, perlite, calcium silicates, silica aerogel,¹⁹² Al extrusion,¹⁹² and graphite composite sheets. However, thermal barriers utilized for TRP prevention should be thermal resistant (>600°C) and have low thermal conductivity (<0.1 W m⁻¹ K⁻¹).²³⁵ Besides, a reliable thermal barrier should maintain the heat insulation area under high-temperature burning and fire impact.²³⁶

Fire extinguishing. As shown in Figure 8R, the typical approaches to fire suppression can be divided into (1) isolation, (2) smothering, (3) cooling, and (4) chemical suppression. Unlike typical fires, some battery fires result from direct reactions between the components. These reactions do not require external oxygen.

A detailed discussion of the fire extinguishing studies is provided in the [supplemental information](#). Table S3 compares the characteristics and critical standards of commonly utilized extinguishing agents for battery fire disasters that guide fire suppression designs for battery systems. Table S4 summarizes the TR/TRP mitigation strategies for high-temperature hazards at the material, cell, and system levels.

CONCLUSION

As the primary obstacle for large-scale LIB applications, thermal issues remain challenging to address, especially for all-climate applications and severe operations, such as fast charging. This study comprehensively reviews the thermo-electric characteristics and mechanisms in all climate areas. To enhance performance and ensure safety in all-temperature areas, advanced thermal management and fire suppression strategies for LIBs have been introduced from the perspectives of subzero, normal, and high temperatures. In addition, as demonstrated in Figure 10, to further address the all-temperature area thermal issues, promising future strategies are provided from the perspectives of the material, cell, and system levels, which include novel material preparation, battery cell design, battery thermal management, warning, and fire suppression technologies (provided in the [supplemental information](#)).

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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