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A review on research status and key technologies of battery thermal management and its enhanced safety

Yan Wang²  | Qing Gao^{1,2} | Guohua Wang^{1,2} | Pengyu Lu² | Mengdi Zhao² | Wendi Bao²

¹ State Key Laboratory of Automotive Simulation and Control, Jilin University, Changchun, China

² College of Automotive Engineering, Jilin University, Changchun, China

Correspondence

Guohua Wang, State Key Laboratory of Automotive Simulation and Control, Jilin University, 130025 Changchun, China.
Email: wanggh@jlu.edu.cn

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Summary

The reliable protection of personal safety and vehicle service security has aroused the rising attention on battery thermal safety issues. This poses ongoing challenges for battery thermal management (BTM) to improve the safety by constantly learning and adopting advanced technologies from thermal management to thermal safety control. On the basis of electrochemical, mechanical, and thermo-kinetic characteristics of battery behavior evolution under operational conditions of normal and abnormal, BTM with enhanced safety cannot only guarantee the battery operation performance but also improve thermo-safety behavior with the heat transfer intensifying method. Additionally, via effective measurements to detect and warn the battery behavior evolution characteristics, the combination of emergency cooling, fire extinguishing, and thermal barrier adopted in BTM with enhanced safety can effectively and sufficiently suppress battery thermal overheating and its propagation. As concluded, the synthesized integration of basic BTM and its safety-enhanced treatment can ensure the optimal working temperature range and prevent thermal overheating from propagation. Thus, the BTM system with enhanced safety has been a promising research priority. This article provides a comprehensive review on BTM with enhanced safety aiming to promote the battery application with high energy density, security, and cyclic stability served for electrification and intelligentization of automobiles. In addition, the summary of relevant research status and key technology is dedicated to improving BTM thermo-safe design innovation and collaborative optimization, to fit with the sustainable development needs of the long-term mechanism of energy conservation and green-energy vehicles marketization.

KEYWORDS

battery thermal management, emergency cooling, fire extinguishing, thermal barrier, thermo-safety

1 | INTRODUCTION

Preventing and mitigating environmental damage can be the greatest challenge for the technological innovation and development of the automobile industry.^{1–3} As the sales banning of the vehicle using conventional fuels such

as gasoline and diesel was proposed by European Union in 2011, deadlines for fossil-fueled vehicle manufactures have been announced sequentially by federal governments, municipal governments, and participants in vehicle industries from China, French, British, Norway, and other countries.⁴ Consequently, researches and

applications of green-energy vehicles powered by lithium-ion battery gain the ever booming development.⁵

Given the high energy density and extended cycle life, lithium-ion battery is regarded as the ideal power source of the green-energy vehicle, especially the electric vehicle.^{6,7} The battery life span and working performance can be adversely affected by temperature, especially when it is out of the optimum temperature range.⁸ Battery temperature influences the availability of discharge power, energy, and charge acceptance during energy recovery from regenerative braking.⁹ As the heat generated without effective management, the rising temperature will accelerate the chemical reaction rate and the process of aging and degradation, which will even cause the catastrophic failure.¹⁰ Similarly, if the temperature is too low, the energy density and capacity of the battery will get deteriorated significantly.¹¹ Moreover, the large-scaled format lithium-ion battery is still favored by manufacturers.¹² And it is more vulnerable to adverse effects for larger energy storage, which causes the uniformity of temperature distribution and increases the uncertainty of safety state identification.^{13,14} What is more, temperature variation from module to module within a pack also can lead to the electrical unbalance, which affects battery pack operational performance.¹⁵ With a higher specific energy and high-rates capability, battery would generate a great amount of heat, which is easier to trigger thermal runaway.¹⁶

It was reported frequently that when the battery pack thermal runaway got provoked under extreme operational circumstance of a relative high ambient temperature, mechanical crush, and overcharge/over discharged, a series of electrochemical and exothermic reactions would happen simultaneously.¹⁷ Then flame spark released and it started on a fire. Besides, the battery spontaneously emitted the toxic hydrogen fluoride (HF), phosphorous oxygen fluoride, carbon monoxide, and so on (eg, CO, CO₂, H₂, and CH₄), which also induced environmental problem. To understand battery behavior, evolution characteristics (eg, temperature rise, pressure and stress variation, gas emission composition, voltage and current, and structure deformation), ranged from normal operation to overheated state and thermal runaway, can be significant for determining and warning the critical thermal event via effective measurements. It is urgent for the battery thermal management (BTM) to consider the safety enhancement to improve the ability of battery heat dissipation, ensure the optimal working temperature range, and prevent overheated phenomenon.¹⁸

The United States started earlier to focus on BTM system (BTMS) with its enhanced safety.¹⁹ In 1978, Benham et al²⁰ invented a battery monitor system for thermal overheating, which operated by determining the slope of

charge current and then comparing the slope with a maximum allowable slope. In 1996, Mcshane et al²¹ presented the thermal overheating detection apparatus, which included the circuitry to detect the increase of conductance or a decrease in internal resistance that provided feedback to control charging of the battery. To guard against the thermal safety issues, it is effective to get its thermal behavior measured along with the thermal properties over the temperature range, such as gas generation and composition. Thus, the evolution characteristics of battery thermal runaway can be obtained.²² To promote the battery safety design, Neubauer et al²³ created and verified an electrical-thermal math model capturing characteristics of the battery packs with the external or internal short circuit to evaluate a/the safe state with substantial additional heating. Furthermore, to standardize the management for battery thermal safety, International Organization for Standardization, Underwriters Laboratories of the United States, and the Society of Automotive Engineers have proposed standard items for thermal safety design,²⁴ such as its publication Safety Standard for Electric and Hybrid Vehicle^{25,26} (no. J2929-2013). It should be noted that the BTM with enhanced safety design should take consideration of the assembly including cells, modules, and packs, besides, coordinate this related machine system, the supplementary system, and electronic control systems.²⁷ Consequently, Liu and He²⁸ and He et al²⁹ have been making progress on battery safety materials, as well as system fault diagnosis and identification. Pei et al³⁰ focused on the life span prediction and degradation modeling with state of charge, state of health, and other properties. The authors' research team^{31,32} proposed and established integrated vehicle thermal management systems by liquid circulation with heat pump application for battery preheating and cooling. It can be concluded that the BTM should not only promote the temperature uniformity control but also have functions of warning and treatment of failure. Also, mechanical protection including insulation, sealing, and mounting strength should be improved.³³

To summarize, the BTM enhanced safety could have a three-layer design concept. Firstly, it can ensure battery operation under optimal temperature range. Secondly, it can detect the critical point of battery failures and deliver alarm messages. Finally, as soon as the thermal hazard happened, the treatment can suppress thermal runaway propagation effectively.³⁴

On the basis of the battery behavior analysis of the overall process from heat generated to overheated, BTM with enhanced safety can satisfy the requirements including the guaranteed battery performance with cooling/preheating, the reorganization of overheated status, and sending alerts signals before the thermal runaway onset

time via various advanced measurements. Additionally, it can inhibit battery thermal overheating at the individual cell level and take precautions against the potential for cell to cell propagation through the combination treatments adopted in BTM and its safe enhancement of emergency cooling, flame extinguishing, and thermal barrier. Featured with multilevel, multifunctional, and multiinteraction, it can be inferred that the relevant research status and key technology of BTMS with enhanced safety has been promising for the sustainable development needs of the long-term mechanism of energy conservation and green-energy vehicles marketization.

2 | BASIC TYPES OF BTM

As one of the core technologies to prolong cycle life and usability performance, the BTM is beneficial for Li-ion battery operation at a suitable temperature range with added components and devices.³⁵ The choice of heat transfer medium including air, liquid, phase change material, or any combination has a significant impact on the performance and cost of the BTM, which has its own limitations and merits. As for the commercial electric vehicle, the statistical tables for the BTM system strategies of different commercial vehicle are shown in Table 1. According to the cooling medium, the mainstream BTM usually can be categorized into liquid cooling, air cooling, and refrigerant direct cooling. It should be noted that the refrigerant direct cooling can take advantage of refrigerant (R134a, R410, etc from HVAC) evaporative latent to chill battery pack straightway.^{36,37}

2.1 | Air cooling

Air cooling has its own characteristics, such as simplicity accessories, low cost, and lightweight as well as maintenance convenience. Because of its advantages, air cooling is widely used in commercial electric vehicles. The commercial vehicles of Nissan Leaf, Toyota Prius Prime, Nissan e-NV200, Honda FitEV, Hyundai IONIQ, and so on are typical representatives of air cooling commercial application.^{38,39} It is proposed that air cooling can be categorized into natural and forced convection. The natural convection can allow the inner or external air to pass through the channel to sweep the battery pack.⁴⁰ And the forced convection usually adopts a fan or cooperates with the evaporator or condenser from HVAC to blow the air into the battery enclosure.⁴¹ Compared with forced-air cooling method, the natural convection cooling usually behaves better in sealing and waterproof for its

TABLE 1 BTMS strategies of commercial vehicles

Year	Manufacturing Company	Model Type	Battery Capacity, kWh	BTMS Strategy	Year	Manufacturing Company	Model Type	Battery Capacity, kWh	BTMS Strategy
2007	GM	Chevrolet Volt	16	Liquid cooling	2013	Tesla	Model X	90	Liquid cooling
2008	Tesla	Model S	85	Liquid cooling	2014	Tesla	Model 3	80.5	Liquid cooling
2009	Nissan	Leaf BEV	24	Air cooling	2014	Audi	A6 PHEV	14.1	Refrigerant direct cooling
2009	Ford	Focus BEV	23	Liquid cooling	2015	GM	Chevrolet Spark	19.44	Liquid cooling
2009	Audi	R8 e-tron	90	Liquid cooling	2015	BMW	X5 PHEV	9.2	Refrigerant direct cooling
2009	BMW	i3	33	Refrigerant direct cooling	2016	GM	Chevrolet Bolt	59.4	Liquid cooling
2010	Honda	Fit EV	20	Air cooling	2016	Reynolds	ZOE EV	45.6	Air cooling
2010	Mercedes-Benz	S400 Blue	70	Refrigerant direct cooling	2016	Hyundai	IONIQ	28	Air cooling
2011	Toyota	iQ	12	Liquid cooling	2017	Toyota	Prius Prime	8.8	Air cooling
2011	Proton	Saga FXL EV	15.9	Refrigerant direct cooling	2017	BMW	i8	105	Refrigerant direct cooling
2012	Nissan	e-NV200	45	Air cooling	2017	Volvo	XC90 T8	10.2	Liquid cooling

Abbreviation: BTMS, battery thermal management system.

enclosure without vents opening.⁴² However, sometimes the natural convection cooling is invalid for battery heat dissipation. Thus, it is an effective option to adopt the forced-air cooling, which is used in the Honda FitEV and Hyundai IONIQ.⁴³

With the development of computer numerical simulation technology, conducting experiments are the best way to validate the accuracy of simulated BTM performance. Lu et al⁴⁴ explored the battery forced-air cooling capability on the temperature uniformity and hotspots mitigation with various air flow paths and airflow rates. By orthogonal experiments and computational fluid dynamics simulations, Xie et al⁴⁵ improved the performance of forced-air cooling with the optimized factors of the air-inlet angle, the air-outlet angle, and the width of the air flow channel between battery cells. Wang et al⁴⁶ discussed factors such as different module patterns, fan locations, and intercell distances that influenced the cooling capability of forced air cooling; besides, they recommended the optimized intercell distance and desired structure with fan location on the top.

As reported, the HVAC unit controls the climate of the passenger cabin by regulating the temperature and humidity of circulated air to enhance passenger comfort. As for the air cooling thermal management of battery pack had inconveniences in preheating in cold weather, the researchers proposed the collaborated air cooling for electric vehicle with integration of the subsystems of HVAC system, which can be called the BTM cooperative with vehicle climate control system. Its effectiveness adopted in Toyota Prius was tested by the National Renewable Energy Laboratory,^{47,48} which put battery modules under the rear seat with channel to direct cabin air across the individual modules. This mentioned innovative component design of BTM cooperative with vehicle climate control system to regulate temperature variation was also presented by Ford.⁴⁹ The fresh air was taken through the front of the vehicle and was blown to the front area to circulate about the passenger cabin. The ventilation port was oriented to direct airflow across the battery components, which had a blower unit worked at exhaust port to direct air after being circulated through the battery cooling system.⁵⁰ As the design introduced by Honda,⁵¹ it had a valve with variable opening to switch the flow channel and flow rates according to battery thermal behavior without any expense of the comfort. As presented in Figure 1, by operating valve 1, it alerted the air inlet mode selection. It was able to switch the channel for the air sucked into cooling fan 3, which can be either the ambient air from the ambient air inlet, or the ambient air flow in the HVAC passing through the evaporator/heater, or the cabin air in the vehicle compartment space from an air inlet port.

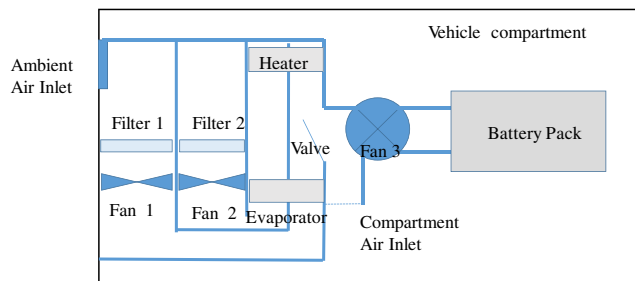


FIGURE 1 Diagram of air cooling coupling with HVAC⁵¹ [Colour figure can be viewed at wileyonlinelibrary.com]

There is no doubt that air cooling is beneficial for toxic gas ventilation, low cost, and lightweighted. But because of a small thermal conductivity of air, the convection heat transfer coefficient between air and battery wall is low. Therefore, sometimes it cannot chill battery efficiently. Also it cannot heat up the battery effectively under low environmental temperature. Thus, to meet thermal control need of battery under complex operational conditions, researchers began to investigate air cooling coupling with HVAC.⁵² It is worth noting that it is a challenge for air cooling coupling with HVAC to satisfy the synthesizing requirements of ensuring battery thermal performance without sacrificing the cabin thermal comfort.

2.2 | Liquid cooling

Compared with air medium, liquid has a higher thermal conductivity and a higher heat capacity, which behaves better in the temperature distribution of battery pack. What is more, it is inevitably related to nonuniform temperature distribution, which can be exacerbated with the increase of battery power density under the climbing or acceleration driving conditions.⁵³ Battery thermal management with liquid circulation loop also has some inconvenience in its complexity structure with some accessories (heat exchanger, pump, etc), and it has potential in leakage. But it has become the prevalent cooling technology in the industrial application, because of its flexibility in integration and precise control for heating and preheating.⁵⁴

2.2.1 | Structural optimization

On the basis of convection heat transfer, the liquid cooling can mitigate temperature rising and prevent battery overheating in virtue of the higher specific heat and thermal conductivity of working medium.^{55,56} To improve the structural design for heat transfer enhancement effectively, a sandwiched structure of BTM usually includes the traction battery, a pair of thermal coolant

plates, and thermal conductivity.⁵⁷ The fins of coolant plate usually have at least 100 W/(m·K) thermal conductivity, extending from the thermal plates into the cells to improve temperature distribution. And to promote temperature uniform distribution on a scale of individual cells, the cooling plates planar was then alerted as Figure 2, which applied with interior fluid serpentine channels allowing coolant flow. But this design always featured with considerable friction loss, so it proposed a BTM relating to a cooling liquid container.⁵⁸ As depicted in Figure 3, the battery module was partially immersed in the cooling liquid such as trichloromethane or trimethyl phosphate, which owned a liquid sealing layer for a protective effect on the battery.⁵⁹ It can be concluded that the liquid cooling structural design usually has three types: cooling fin sandwiched between two cells sitting on coolant plates, cooling tubular plates between cells with interior fluid channels, and directly contact cooling with coolant immersed cells. Wang et al⁶⁰ conducted computational fluid dynamics simulation to assess the three mentioned typical liquid cooling structural designs for a large capacity Li-ion pouch cell. Their simulated

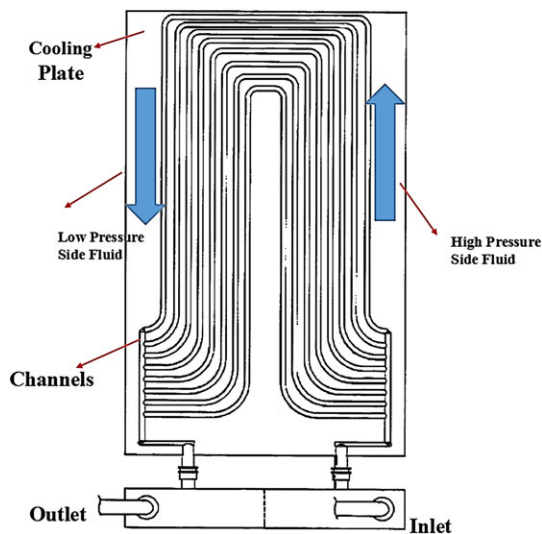


FIGURE 2 Cooling plates planar⁵⁸ [Colour figure can be viewed at wileyonlinelibrary.com]

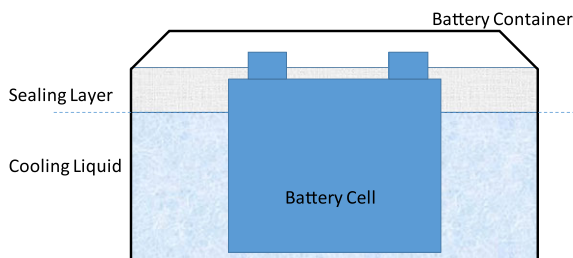


FIGURE 3 Cooling liquid with a battery container⁵⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

results proved that a liquid cooling system with tubes or jacket can get the lowest maximum temperature rise; and a fin cooling system adds about 40% extra weight of cell, which weighs most. Liquid cooling with tubes or jacket is more practical though it has slightly lower cooling performance than liquid cooling with coolant immersed cells.⁴³

Additionally, Teng and Yeow⁶¹ analyzed thermal performances of two battery modules/pack cooling methods with the indirect liquid cooling system of three types of cooling tubular plates between cells with interior fluid, which exhibited in Figure 4. They concluded that the structural layout of multiple parallel-channels cold plate resulted in a lower coolant pressure and temperature gradient. It should be further noted that a deep insight of the thermal-hydraulic interactions and characteristics is the foundation of the liquid cooling system implementation utilization with heat sink. Straubel Jeffrey et al⁶² provided the thermally conductive tube mounted next to batteries to absorb heat from batteries and transfer it to liquid, which was propelled by a pump to a radiator. The radiator can help the heat to be released to the air.

Because the liquid cooling system with heat sink usually uses many thermal-dynamic devices, it is significant for its strategies developing to make the trade-offs among costs, complexity, weight, cooling effects, temperature uniformity, and parasitic power. And the optimize design of integrated vehicle synergy control mechanism and its mode switch should be built up.⁶³

2.2.2 | Coupling with HVAC

With multiple independent mechanical and electrical components distribution, the electric vehicle faces complex thermal management requirements, such as cabin thermal comfort as well as preheating and cooling for the battery pack, power electronics, and electric motor subsystems.^{54,64} Battery electric vehicles are usually installed with mobile air conditioning (MAC) systems to ensure a comfortable indoor climate in all ambient conditions.⁶⁴⁻⁶⁶ And BTM can satisfy the battery thermal demands for preheating and cooling.⁶⁷

In general, an air conditioning (AC) system for an electric vehicle usually uses a separate heater circulating the refrigerant to warm up the cabin coupling liquid coolant for battery pack.⁶⁸ As the energy and power capability of most batteries diminishes at colder climates, the heating system is indispensable. Then, a much more improved design was proposed by GM in its developed commercial electric vehicle “Chevrolet Volt,” which used the three-way valve to selectively direct the coolant flow routine according to battery heating and cooling requirements.³¹ As shown in Figure 5, path “A” can satisfy the

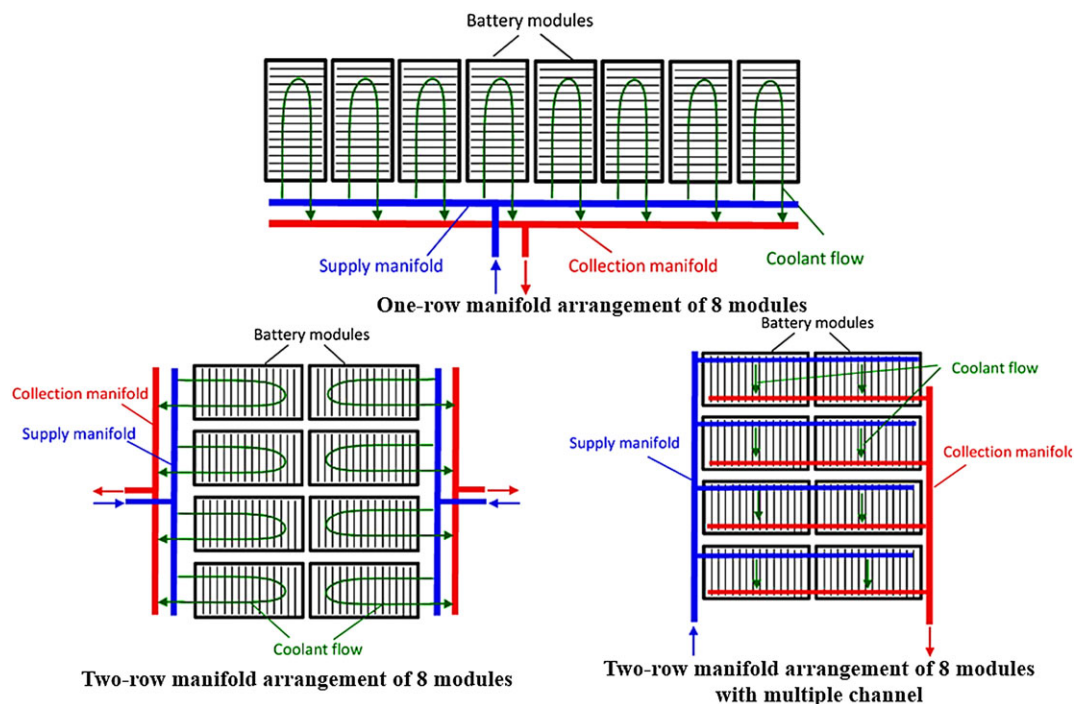


FIGURE 4 The liquid cooling system of three types cooling tubular plates⁶¹ [Colour figure can be viewed at wileyonlinelibrary.com]

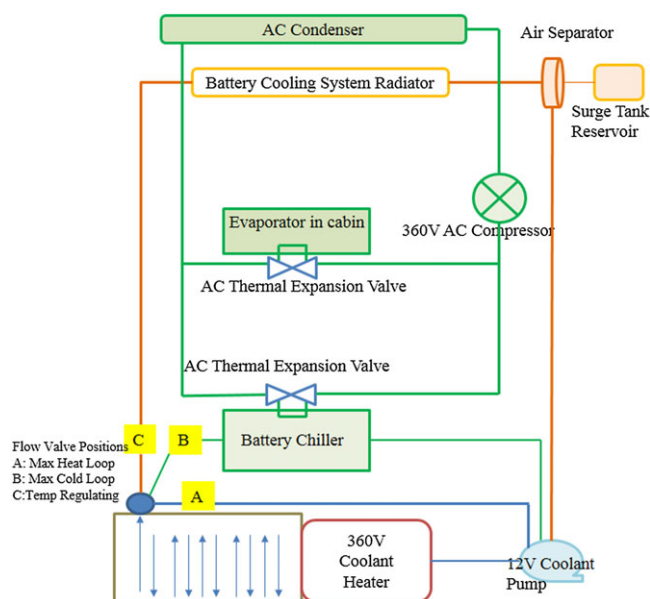


FIGURE 5 Battery thermal management of “Chevrolet Volt”³¹ [Colour figure can be viewed at wileyonlinelibrary.com]

need for batteries preheating. And path “B” permitted cooling coolant dissipated heat to refrigerant of HVAC via the chiller to suppress overheating. At last, under normal driving circumstance, the valve usually switched to path “C” allowing battery cooling with radiator.³¹ To meet the demands of heating and cooling for the passenger cabin and battery pack, Malik et al⁶⁹ provided a simplified BTM coupled with HVAC system. During normal

operation, the coolant was contained in cooling loop via heat transfer with the refrigerant in the heat exchanger. Additionally, cooling loop is also thermally coupled to a heater, eg, positive temperature coefficient, thus insuring that preferred operating temperature can be maintained regardless of the low ambient temperature.⁷⁰

What is more, the heat pump system can be switched from heating to cooling by controlling the chiller operation to replace the application of the positive temperature coefficient or the heater, which can supply adequate heating/cooling capacity for the liquid coolant.⁷¹ Thus, the size and weight of a BTM for battery module can be reduced in place of the heater.⁷² Additionally, BTM with a heat pump is an efficient trade-off between functionality, weight, mechanical complexity, and various thermal requirements. Hamut et al³⁷ and Zou et al⁷² assessed the two different BTM systems of air cooling assisted with cabin climate control system and the liquid circulation via HVAC. Then Cao et al⁷³ pointed out that the BTM used a heat pump owned the superiority for real-time warming up and energy conservation. It can be concluded that a vehicle battery cooling system integrated with a heat pump can effectively simplify the mechanical structure of the entire system, reduce manufacturing cost, what is more, improve the weight and spatial utilization.⁷⁴

Liquid circulation cooling usually behaves better in temperature controlling and uniformity. And it is beneficial to prolong the electric vehicle driving range. It can satisfy various thermal controlling requirements not only

for battery but also for power electronics and electric motor subsystems according to different temperature control demands with the multiple fluid loop mechanism. What is more, it should be noted that the communications shared between passenger thermal comfort and battery thermal performance in the degree of the thermohydrodynamic-mechanical interaction need further investigations. And, the performance and usability of the integrated electrical vehicle in the collaboration with battery cooling system and HVAC system (heat pump system) should be improved.

2.3 | Refrigerant direct cooling

As the forced-air cooling coupling with HVAC has advantages in mechanical structure, however, because of the low thermal conductivity of air, it is insufficient sometimes.⁷⁵ As for the aforementioned liquid cooling with HVAC, the first coolant loop for battery is usually connected with the secondary refrigerant circulation loop with the joint of the intermediate refrigerant-coolant heat exchanger, which adds weight and complexity of the system.⁷² Breaking limitations in system complexity usually resulted in inconvenient coordinated control of liquid cooling with HVAC, and then the refrigerant-based direct cooling was raised.

As illustrated in Figure 6, Wang et al¹⁰ compared the typical refrigerant-based direct cooling and the BTM composed of liquid cooling with HVAC. The direct refrigerant cooling featured with a separator refrigerant, a transportation channel of refrigerant, and a pump elimination, and it behaved better in heat transfer efficiency, temperature uniform distribution, simplified structure, and system weight reduction.⁷⁶ In conclusion, for its efficiency in thermal control and heat dissipated ability, and avoiding cooling medium leakage, it can definitely improve the systems performance matching and has been a promising strategy for BTM design.^{77,78} There usually exists two parallel branches of the HVAC refrigerant systems: One is the direct refrigerant battery cooling branch, and the other is to immerse the battery in the refrigerant. Weileder et al⁷⁹ invented this battery pack casing of BMW i3 equipped with the expansion valve and globe valves to operate independently the fluid overheating degree and import/export,

respectively. After the expansion valve, the liquid (or partly liquid) refrigerant will flow into the evaporator to cool the battery directly via a lot of evaporative latent heat.

Considering thermal control and heat transfer enhancement, the refrigerant direct cooling has gained an increasing attention for its large evaporative latent compared with air, coolant (water and glycol), or other cooling medium.⁵⁰ The refrigerant direct cooling usually has two different structural designs. One is the cooling plate utilization with interior channels, which are identified to be an evaporator of AC refrigerant system. The other one is to immerse the battery in the saturated liquid refrigerant. Functioned as an evaporator, the design of cooling plate within refrigerant has found a widespread acceptance and understanding. Nemesh and Guerin⁸⁰ presented BTM for a battery pack having a direct cooling plate with internal cavity for refrigerant freely flowing. To achieve the compact and integrated system, space savings, and lightweight, LG developed the BTM of direct cooling with exemplary refrigerants⁸¹ of R11, R12, R22, R134a, R407C, and R410A. Additionally, the diagram and feature of direct refrigerant cooling at different levels of cell, module, battery pack, and multiple system integration can be outlined⁸²⁻⁸⁵ in Figure 7. An et al⁸⁶ investigated a new type of refrigerant direct cooling based on the mini-channel that used a hydrofluoroether liquid with a boiling point of 34°C; the experimental setup was shown in Figure 8. It was illustrated that the maximum surface temperature difference of battery monomer could be reduced about 4°C because of the advantages of boiling heat transfer. As well as temperatures of battery cells were maintained around 40°C with boiling heat transfer method.⁸⁷⁻⁹⁰

Moreover, another common mean of BTM with refrigerant direct cooling is to immerse the battery in the saturated liquid refrigerant. Compared with evaporator plates, this method has defected in system sealing and leak. Al-Zareer et al⁷⁷ investigated the boiling process intensity with decreasing the pressure and obtained the principle that the boiling process can be actively and rapidly controlled by regulation of the pressure in the boiling chamber. Additionally, the typical application was proposed by Eisenhower,⁹¹ as illustrated in Figure 9. The direct refrigerant cooling system included a chamber contained the saturated liquid R134a or HFO1234yf

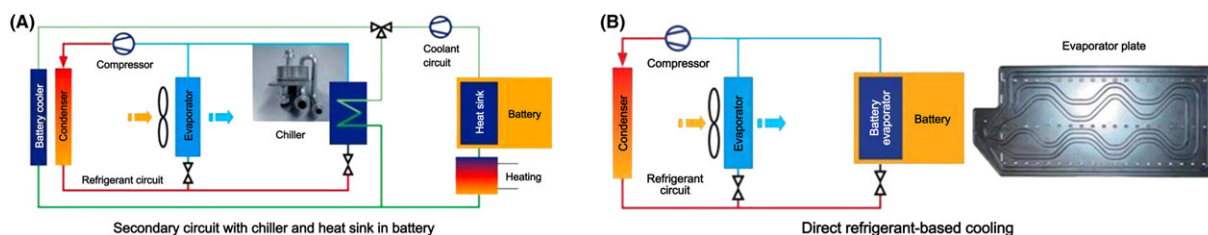


FIGURE 6 Different battery thermal management strategies¹⁰ [Colour figure can be viewed at wileyonlinelibrary.com]

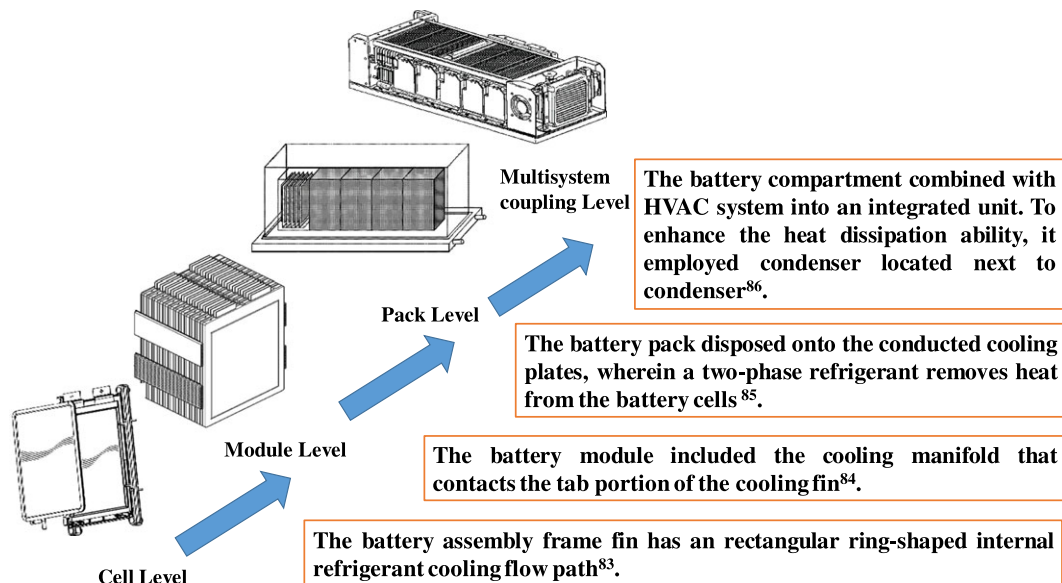


FIGURE 7 Outline of the feature refrigerant direct cooling at different levels⁸²⁻⁸⁵ [Colour figure can be viewed at wileyonlinelibrary.com]

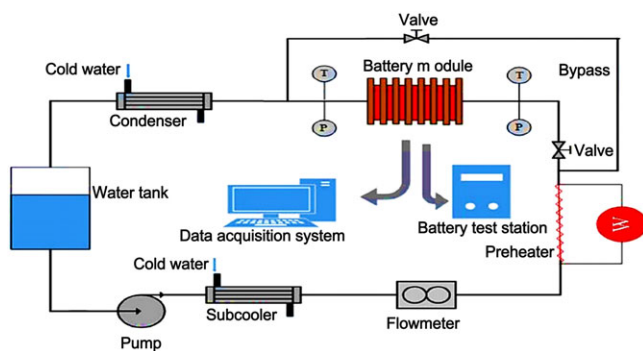


FIGURE 8 The refrigerant direct cooling with the mini-channel⁸⁶ [Colour figure can be viewed at wileyonlinelibrary.com]

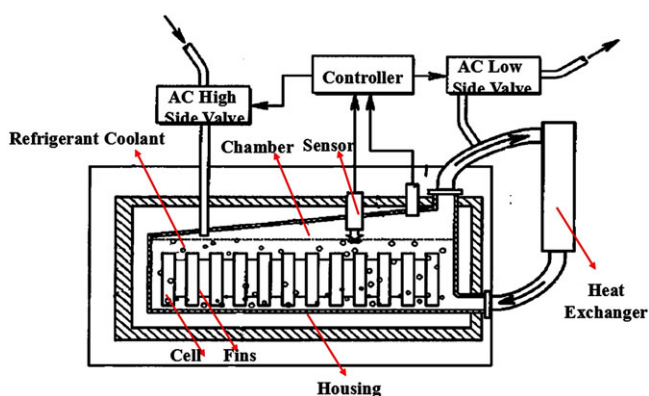


FIGURE 9 The typical application of refrigerant direct cooling system⁹¹ [Colour figure can be viewed at wileyonlinelibrary.com]

submerged the battery module with their cooling fins. The low side valve was operable to receive the vapor phase coolant from the chamber and connected to a low

pressure side of the AC refrigerant system. The high side valve was to provide the liquid phase coolant from a high pressure side of the AC refrigeration system to the chamber. The suitable temperature threshold was set as 45°C, and the pressure threshold was defined as 1100 kPa. Acting in accordance with the controller threshold, the operation of the compressors in the AC system can pump coolant into and out of the chamber. Additionally, in 2018, Tajima et al⁹² provided a battery device for its outer surfaces contacting with evaporative cooling coolant, as shown in Figure 10. And the temperature change of the battery can be maintained at a temperature closed to the boiling value of cooling liquid during battery operation.

As concluded, refrigerant direct cooling with boiling heat transfer has several significant advantages in higher

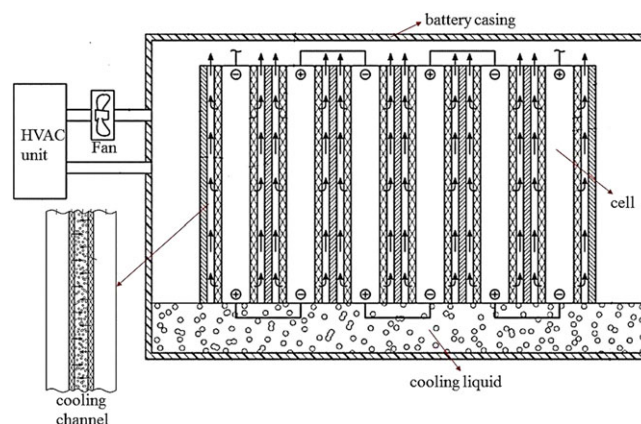


FIGURE 10 Refrigerant direct cooling system of the battery thermal management application⁹² [Colour figure can be viewed at wileyonlinelibrary.com]

heat fluxes with evaporative latent heat, better thermal homogenization for temperature uniform distribution, and compact structure with eliminating a pump mechanism, as well as a more rapid thermal response compared with conventional BTM. Therefore, it can be an excellent strategy for a high necessity of battery thermal safety.^{31,77} Additionally, it also can be applied to battery thermal safety synergy control for its potential in emergency cooling of spaying and prevention overheating or thermal runaway propagation. It means that refrigerant-based direct cooling should develop a cross-coupling controlling strategy to realize the synergy control both for BTM and BTM with enhanced safety.

3 | R&D OF BTM WITH ENHANCED SAFETY

With the development trend of high capacity and large scaled-format application, battery suffers safety problems from heat generation rates rise, battery aging, and degradation acceleration, which can worsen the stability and life span.^{3,93} Thus, to guarantee personal safety and automobile service security, attention has been aroused on BTM to enhance the safe treatment.^{94,95} As shown in Figure 11, the consideration should be taken not only to ensure the optimal working temperature range with BTM but also to prevent overheating and thermal runaway. With thermal safety management through the synthesized combination of reorganization critical point via effective sensor, the safety status can be determined on

the basis of a well understanding of battery overheated behavior characteristics.

3.1 | Overheating behavior characteristics

The BTM with its safety enhancement should switch its controlling mode according to the different demands; that is to say, the thermal/electrical/biochemical thresholds should be set in advance. Thus, battery model to describe battery thermo-electrical-chemical behavior needs to be established. And it will provide a significant reference for BTM and its safety decision making to improve its feasibility and practicality. What is more, understanding the behavior characteristics rules in the whole evolution from normal operation to thermal runaway can be critical to define the safety status for thermal safety management.

3.1.1 | Experimental investigation

The evolution of the battery from normal operation to thermal runaway can be identified as a self-heating and spontaneous combustion process with great amount of heat release. Thus, the variation of temperature, resistance, and voltage, as well as the maximum temperature and the onset temperature rate, can be excellent judgment for battery evolution. Consequently, to evaluate lithium-ion cell stability and reliability, researchers usually took safety tests such as hot oven tests and nail penetration tests into consideration.³² For example, a hot oven test can heat the cell at speed of 5 K/min under adiabatic thermal condition to trigger overheating or thermal runaway. With different nail penetrated depth, nail penetration tests can analyze different cell short circuit situations including short circuit between anode and cathode current collectors, anode current collector and graphite negative electrode, positive electrode materials and cathode current collector, and negative and positive electrode. These tests can definitely provide critical information of cell thermal/electrical/chemical behavior, which is significant to guide the design for BTM with its safety control.

Feng et al and Ouyang et al⁹⁶⁻⁹⁹ provided a comparative study on the thermal runaway mechanisms under overheated thermal abuse condition. When the battery was under thermal runaway, the voltage sharp drop would happen and the internal resistance would rise to 370 mΩ indicating the melting of the separator and serious internal short circuit occurrence. The temperature reached to the highest value of 870°C just in 15 to 40 seconds. According to these, they divided the thermal runaway process into six exothermic reactions stages: solid electrolyte interface (SEI) decomposition, reactions of the anode, the cathode decomposition, the electrolyte decomposition, the separator melting, and the massive

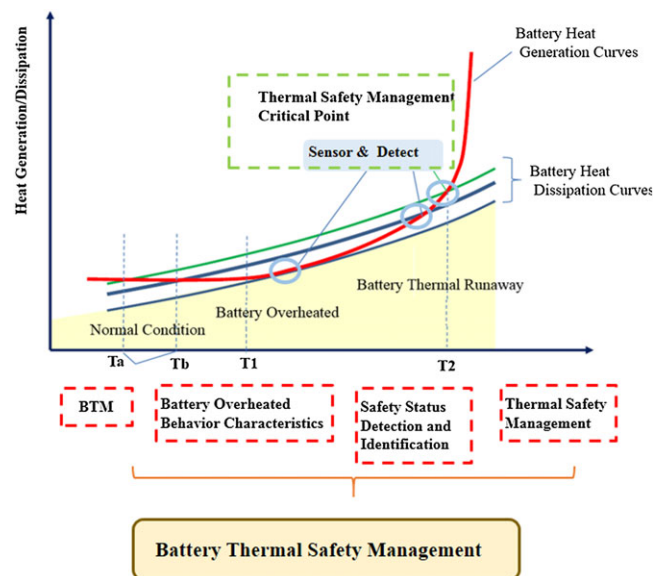


FIGURE 11 Diagram of battery thermal management with safety enhancement [Colour figure can be viewed at wileyonlinelibrary.com]

internal short circuit. It should be noted that the internal resistance increased slowly from 20 to 60 m Ω before thermal runaway, which can be made use for battery safety detection and identification. Besides, thermal runaway can be induced by other unexpected abusive conditions such as mechanism crush and over discharging/charging.^{87,100} Additionally, confronted the bumpiness, the battery connection accessory and its mounting structures may be twisted and deformed, thus inducing severe internal or external short circuit.⁸⁸ Therefore, various mechanical tests were performed to characterize failure behavior of lithium-ion cell and its components.⁸⁹ Such safety tests of nail penetration internal short circuit test and external short circuit test were performed⁹⁰ from earlier 1990s. Through wiring the current collectors of batteries together with different external resistors, Hong et al¹⁰¹ analyzed a mass of electrolyte vapor released when the value of external resistance equals to the battery internal resistance.

Experimental investigation also goes to the thermal overheated propagation from cell to cell. Ren et al¹⁰² used thermal runaway risk score assessment to distinguish commercial Li-ion cell safety stability in the pinch and the pinch-torsion test. Finegan et al¹⁰³ tracked the process of internal structural damage including gas-induced delamination and electrode layer collapse to get a deeper insight of battery degradation evolution. The results were

measured by the application of high-speed synchrotron X-ray computed tomography and radiography, in conjunction with thermal imaging. Figure 12 completely reveals the destruction of the cell in original spiral-wound architecture. The presence of the large copper globules with temperature reached in excess of 1085°C denoted melting of anode, which were highlighted in yellow. To study the thermal failure spread to neighboring cells, Lamb et al¹⁰⁴ tested 18 650 cells connected in series and parallel and found the electrical connectivity to be impactful for thermal runaway. Compared with the 10S1P cylindrical cell module, the 1S10P module underwent an energetic thermal runaway and got a higher temperature.

To avoid the continuous exothermic reactions resulting in catastrophic failure such as fires and explosions, it is expected to prevent thermal hazard by using the additional external intervention including pressure relief vents,¹⁰⁵ positive temperature coefficient devices,¹⁰⁶ and current interruption device.¹⁰⁷ The safety external intervention can control the commercial battery out of operating after thermal overheating. Besides, from the point of cell materials innovation, the presence of a heat-resistant ceramic powder with a high surface area¹⁰⁸ and a hydrophilic polymer binder¹⁰⁹ as well as the ceramic-coated separator,¹¹⁰ etc, also exhibited good thermal stability and cycling performance.

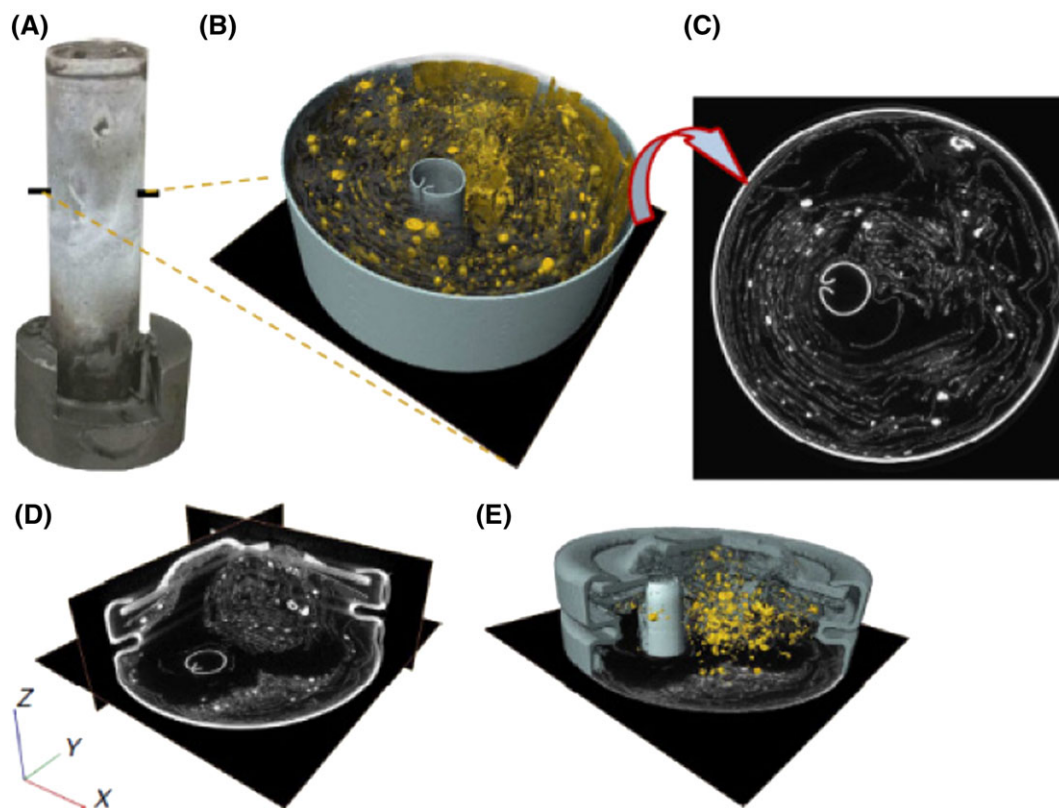


FIGURE 12 The battery degradation evolution²³ [Colour figure can be viewed at wileyonlinelibrary.com]

3.1.2 | Simulation modeling and analysis

There have been a number of efforts on thermal modeling of lithium-ion battery varying in complexity from a one-dimension simulation to a three-dimension modeling. In 1984, Bernardi et al.¹¹¹ firstly introduced the one-dimension general energy balance equation to depict the temperature changes as a result of electrochemical reactions and joule heating. Kim et al.¹¹²⁻¹¹⁴ reported a two-dimensional modeling method of the potential and current density distribution on the electrodes. Concerning about the Li-ion transport phenomena in the porous electrode and electrolyte, a three-dimension thermal/electrical/electrochemical coupled modeling of lithium-ion battery coupling with porous electrode, mass conservation laws, and concentrated solution theories to accurately capture Li-ion migration in the battery was developed.^{115,116} However, these models studied the behavior under normal operation extensively, which has limitations for describing mechanisms and abuse characteristics during the evolution process from normal operation to battery overheated and even thermal runaway.

Considering battery abusive experiments destined to be time-consuming and costly, thus, the numerical simulation is alternative to predict battery characteristics including temperature, current, voltage, resistance, and heat generation regime.¹¹⁷ On the basis of the theory of heat transfer, chemical reaction kinetics, and electrochemistry, the simulation modeling can be established to illustrate the battery abuse tolerance and its thermal behavior.⁹⁸ This methodology can support the design for an abuse-tolerant Li-ion battery system and improvement of BTM with its thermal safety enhancement.¹¹⁸

3.1.3 | Thermal safety of cell

To illustrate Li-ion battery heat transfer mechanism and thermal behavior during the whole processes from normal operation to thermal overheated or even thermal runaway, a considerable number of researches and explorations have been conducted. As shown in Table 2, the mathematic models established from different perspectives can be the useful references for the designer and BTM application.

According to the Arrhenius theory and Newton law of cooling, in 1958, Anderson¹²² expressed the relationship between battery system internal heat generation/discharging rates and temperature variation, as shown in Table 2. With advances in experimental research, thermal stability performance has been revealed with different materials for the electrode and electrolyte and the SEI.¹²³ As for Dahn's mathematical model, the electrochemical and exothermic reactions kinetics can be put

into three sections: decomposition of SEI layers, as well as anode and cathode reaction with electrolyte proposed by Yayathi et al.¹²⁴ Then, on the basis of this research, Kim et al.¹⁷ extended a three-dimension model considering the four categories reactions with supplemented electrolyte decomposition, as shown in Table 2. Once thermal runaway occurred, Li-ion cells would eject electrolyte vapor accompanied by some flammable gases. To consider this phenomenon, a lumped model with analyzing electrolyte evolution during thermal runaway involved with evaporation, boiling, and venting was presented by Coman et al.¹²⁵ As summarized in Table 2, electrolyte ejection was assumed to be an ideal gas isentropic flow passed through an orifice when the pressure inside reached a critical pressure of 3448 kPa, which showed good agreement with experiments.

By analyzing the heat generation, gas production, SEI film decomposition, and reaction between lithium and electrolyte during the evolution from lithium-ion battery normal operation to overheating and even thermal runaway, a method to define the overheat status of a battery was proposed by Zhao.¹²⁶ This research got the heat generation variation curves of heat generation and temperature variation under adiabatic condition work and then established a thermo-genic model for the 18650 cell with capacity of 2600 mAh to predict the temperature variation. The heat generation curves of SEI film decomposition and the lithium and electrolyte reaction are shown in Figure 13A. And the temperature variation can be shown in Figure 13B. Zhao also pointed out that when battery confronted the abusive condition, the secondary reaction induced the temperature increasing exponentially, and the temperature would reach to 125°C at 4000 seconds. Additionally, to study multiphysics electrochemical phenomena within a cell, Xia et al.¹²⁷ developed a mechanical-electrical-thermal model to simulate the force displacement response of the indentation process, which induced the electric short circuit of individual cell and shell casing, as shown in Figure 14. Chao et al.^{128,129} presented a sequentially coupled mechanical-electrical-thermal modeling approach with the precise geometry of the cell with layers of separator and electrode and analyzed the mechanism abuse tolerance. This approach can be explicit representations from different physics at different scales for each component such as the active material, current collector, and separator.

3.1.4 | Overheating propagation within modules

After the single cell failure is triggered, then it quickly causes much more heat, extensive collateral damage, and even severe consequence to the surrounded cells

TABLE 2 Different simulated modes

Model	Nebiker and Pleisch ¹¹⁹	Kenji and Yoshio ¹²⁰ and Mcshane et al ²¹	Raghavan et al ¹²¹
Equations	<p>(1) System heat release rate: $q_G = \Delta H M'' A \exp\left(-\frac{E}{RT}\right)$</p> <p>(2) System heat dissipation rate: $q_L = US(T - T_0)$</p> <p>(3) Heat generation: $\dot{q} = q_G - q_L$</p>	<p>(1) SEI decomposition: $\frac{dc_{seil}}{dt} = -A_{seil} \exp\left[-\frac{E_{seil}}{RT}\right] c_{seil}^{\mu_{seil}}$</p> <p>(2) Cathode reaction with electrolyte: $\frac{dc_{ne}}{dt} = -A_{ne} \exp\left(-\frac{t_{seil}}{t_{seil,ref}}\right) \exp\left[\frac{E_{ne}}{RT}\right] c_{ne}^{\mu_{ne}}$</p> <p>(3) Anode reaction with electrolyte: $\frac{dc_{pe}}{dt} = A_{pe} \exp\left[-\frac{E_{pe}}{RT}\right] \alpha^{\mu_{pe,1}} (1-\alpha)^{\mu_{pe,2}}$</p> <p>(4) Electrolyte decomposition: $\frac{dc_e}{dt} = -A_e \exp\left[-\frac{E_e}{RT}\right] c_e^{\mu_e}$</p> <p>(4) Heat generation: $\dot{q} = H_{seil} W_{seil} \left \frac{dc_{seil}}{dt} \right + H_{ne} W_{ne} \left \frac{dc_{ne}}{dt} \right + H_{pe} W_{pe} \left \frac{dc_{pe}}{dt} \right + H_e W_e \left \frac{dc_e}{dt} \right$</p>	<p>(1) Cathode reaction with electrolyte: $\dot{Q}_{ne} = M_{ne} h_{ne} \frac{d\chi_{ne}}{dt}$</p> <p>(2) Anode reaction with electrolyte: $\dot{Q}_{pe} = -M_{pe} h_{pe} \frac{d\chi_{pe}}{dt}$</p> <p>(3) SEI decomposition: $\dot{Q}_{seil} = -M_{seil} h_{seil} \frac{d\chi_{seil}}{dt}$</p> <p>(4) The heat generated due to electrochemical reactions: $\dot{Q}_{electrode} = -(M_{pe} + M_{ne}) h_{electrode} \frac{d\chi_{soc}}{dt}$</p> <p>(5) Heat dissipated during venting of the electrolyte: $\dot{Q}_{vent} = -M_e h_{vap} \frac{dy}{dt} - M_e c_{p,e} T \frac{dy}{dt}$</p> <p>(6) The heat absorbed during the boiling of the electrolyte: $\dot{Q}_{boil} = M_e h_{vap} \frac{dP}{dt} - v_{h,i} \frac{dP}{dt}$</p> <p>(7) The heat contribution due to electrolyte venting of the eject: $\dot{Q}_{ej} = -M_{ej} c_{p,jr} T \frac{dy}{dt}$</p> <p>(8) Thermal energy: $\dot{Q} = \dot{Q}_c + \dot{Q}_a + \dot{Q}_s + \dot{Q}_e + \dot{Q}_{ec} + \dot{Q}_{vent} + \dot{Q}_{boil} + \dot{Q}_{ej}$</p>

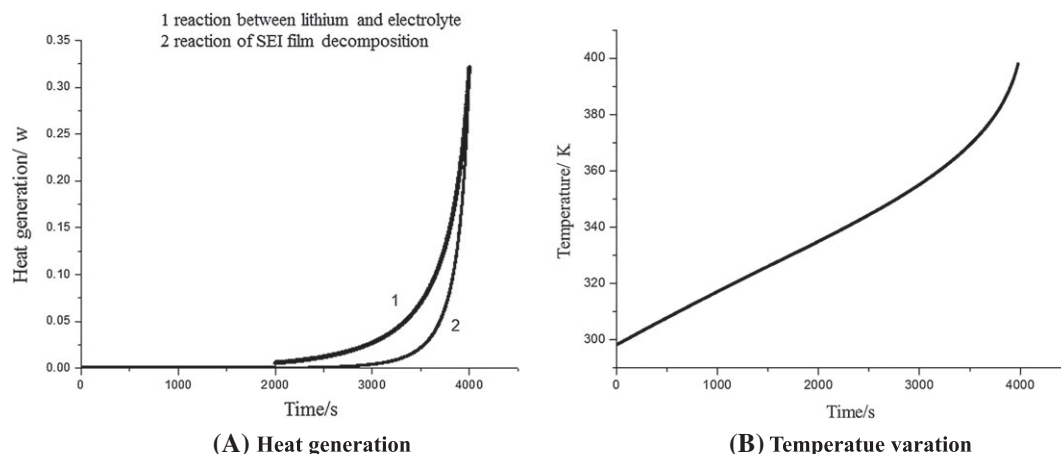


FIGURE 13 Results of Zhao¹²⁶

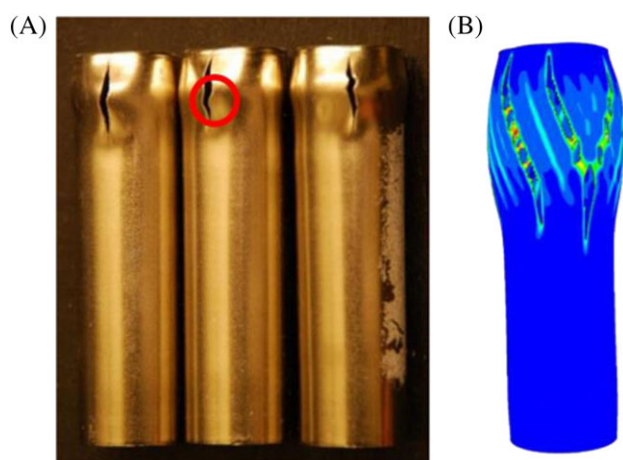


FIGURE 14 Electric short circuit of cell and shell casing^{128,129}
[Colour figure can be viewed at wileyonlinelibrary.com]

dramatically, leading to propagation.¹³⁰ Neubauer et al²³ have developed a 3D electrochemical/electrical/thermal model called multiscale multidimensional modeling approach with the presentation of the thermal runaway propagation characteristics of cell capacity, chemistry, and type of assembly. Larsson et al¹³¹ predicted the cell-to-cell fire propagation induced by thermal runaway, and the flames evolution and its temperature variation are shown in Figure 15. From 2015, Xuning et al^{98,132} began to focus on establishing the thermal runaway propagation model to guide the safety design of the lithium-ion battery pack. According to Figure 16, the thermal runaway propagation from battery no. 1 to no. 2 led to a higher temperature in no. 2 and caused a much faster thermal propagation from battery no. 2 to no. 3. Then, Coman et al¹³³ analyzed the heat propagation during thermal runaway in a battery pack triggered by an internal short circuit by a 2D Finite Element Analysis (FEA)

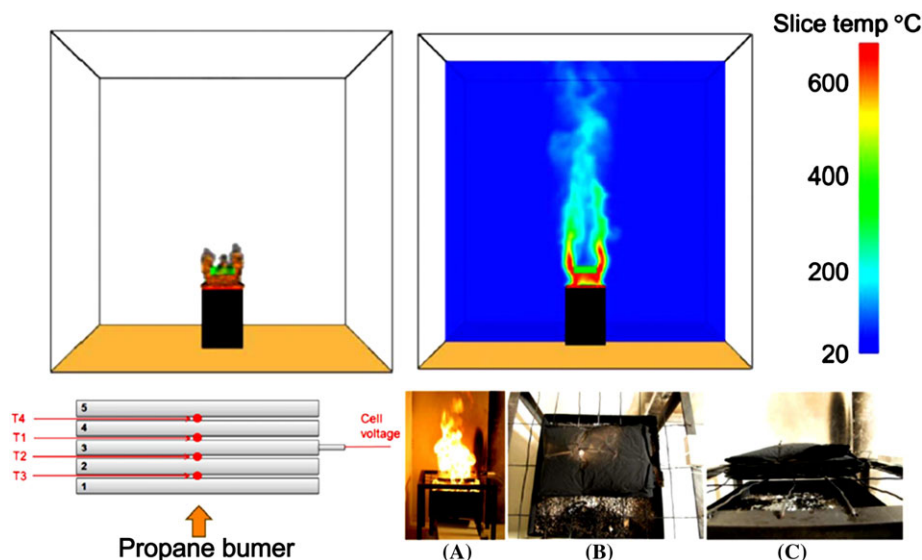


FIGURE 15 Fire propagation experimental results¹³¹ [Colour figure can be viewed at wileyonlinelibrary.com]

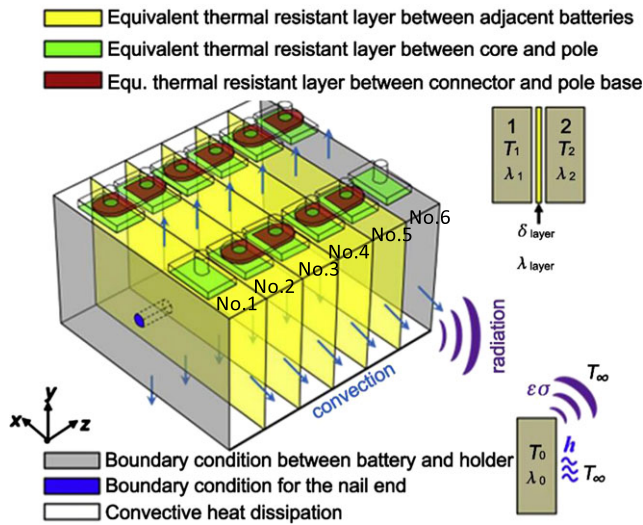


FIGURE 16 Thermal runaway propagation simulation results^{98,132} [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

thermal and electrochemical coupled model. Through the analysis of temperatures differences, the gas temperatures, and heat transfer coefficients, a combination of small insulating layers wrapped around the cells with a conductive heat sink was beneficial to mitigate thermal runaway propagation.

3.2 | Safety status detection and identification

Aim to recommend an efficient thermal management with safety strategy, it calls for an accurate diagnostic analysis system with real-time monitoring of the behavior characteristics during the battery overall operating states to provide the information about the battery safety status and warning when the presetting abnormal threshold has been exceeded.¹³⁴ Thus, status detection and identification providing a benchmark for thresholds presetting can reinforce the BTM with its enhanced safety design.¹³⁵

3.2.1 | Thermoelectric parameter

As known to all, temperature monitoring is an effective and feasible way to detect battery performance directly.¹³⁶ Mutyala et al¹³⁷ inserted a flexible polymer-embedded thin-film thermocouples in a lithium-ion battery cell for in situ temperature monitoring at different charge and discharge cycles. However, the location of temperature measurement can definitely affect the temperature distribution evaluation and its safety status judgment.²² Thus, Lee et al¹³⁴ examined three different spatial variations of thermocouples distribution for temperature measurement, which included (1) temperature sensors located outside the cell, (2) temperature sensor mounted on top

of the cell and sealed inside, and (3) the sensors inserted deeply into the cell.

As another characteristic easy to be measured directly, voltage and current variation can be captured through an integrated microsensor of micro-electro-mechanical systems, which contributed to the early fault diagnosis prediction.¹³⁸ It can be concluded that battery cell parameters of temperature, voltage, and current are all the typical real-time and direct monitor system.¹³⁹ However, such measurement accuracy and reliability are usually highly depended on sensors location and distribution. With advances on developing technique served to improve the battery safety and performance, the indirect measurement with optical fiber Bragg grating (FBG) sensors identified as the representative has been the researching focus.¹⁴⁰ Weston et al¹⁴¹ provided the fiber optic detecting apparatus application, as shown in Figure 17. When the cell temperature increased beyond a certain threshold of the system controller, the transmission quality of optical fiber got altered leading to a change in the intensity of the light transmitted through fiber from the source to detector and BTMS controller to provide signals for other subsystems.

As reported, FBG sensors had advantages in immune to electromagnetic interference, nonconductive, and chemically inert. As for their small size, flexibility, and monitoring multiple points simultaneously at the same time, they were firstly introduced for temperature measurement of fuel cell.¹⁴³ There is no doubt that it can be an excellent method to describe electrochemical, mechanical, and thermo-kinetic interactions among Li-ion cells.¹⁴⁴ Compared with thermocouples, FBG sensors cannot only monitor battery temperature variation but also record the local static and fluctuating pressure, refractive index, strain, and bending degree under normal/abnormal conditions.^{142,145}

3.2.2 | Biochemical parameter

Furthermore, gas development inside battery cells is a well-known phenomenon indicating the failure of a battery.¹⁰³ As concluded, gas generated slowly with increasing temperature at the initial stages. But a sudden

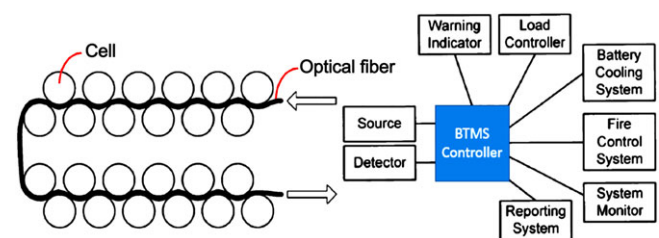


FIGURE 17 FO detecting apparatus¹⁴² [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

increase would occur with releasing of CO and CO₂, indicating decompositions of the cathode and electrolyte, which can be measured by Fourier-transform infrared spectroscopy gas measurements.^{146,147} What is more, it gets much more worsen when cell ejecting the flammable electrolyte vapors.¹¹⁹ Thus, the discharge of different compositions of toxic gas with heavy smoke is expected to be a valuable reference for real-time monitoring embedded by BTM and its safety control system.¹⁴⁸

With the protective design, once gas sensor detected the leakage vapor of electrolyte, the controller can stop the charge or discharge operation as soon as possible. Kenji and Yoshio¹²⁰ invented the battery leakage detection system composed of a gas sensor for testing saturated vapor of ethylene carbonate and propylene carbonate. Additionally, Raghavan et al¹²¹ proposed an innovative BTM to determine the normal and abnormal states based on sensing the amount of CO₂ and hydrocarbon gas, as illustrated in Figure 18. The normal state can be determined when the amount of CO₂ and hydrocarbon gas was less than the threshold of the 3 and 6 mL, respectively. When the amount of CO₂ exceeded the threshold of 3 mL and the amount of hydrocarbon gas remained below the threshold of 6 mL, it indicated the cell at a state of overcharged. Moreover, if the amount of hydrocarbon gas was larger than the threshold of 6 mL, the cell was over discharged. It should be noted the cell internal short circuit can be detected as the CO₂ amount was above the setting threshold of 27 mL and hydrocarbon gas was larger than the threshold of 6 mL. Thus, gas and smoke monitoring unit is very useful to timely alert of safety status. Yuan et al¹⁴⁹ from Shandong Electric Power Research Institute of China provided the cloud computing technology application for an electric vehicle safety early warning system. It can realize data cloud synchronization according to battery behavior characteristic monitoring in both thermoelectric and biochemical parameters.

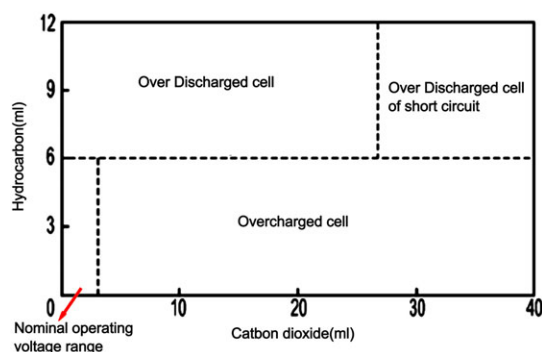


FIGURE 18 The controller threshold presetting battery thermal management¹²¹ [Colour figure can be viewed at wileyonlinelibrary.com]

To construct an accurate diagnostic analysis system, battery management system should cooperate with BTMS. With real-time monitoring of the battery performance in overall operating states, it can judge battery damage, aging, and module degeneration and warn when the presetting abnormal threshold has been exceeded. The battery status detection and identification have great significance for its performance analysis and sending warning for abnormal operating of electric vehicles. Thus, because the monitoring system has high practicability and reliability in detecting the hidden trouble, it can improve the public safety and vehicle security, as well as prolong the rescue time for thermal hazards. What is more, a timely and precise monitoring system can also satisfy the need for intelligent connected vehicle development.

3.3 | Thermal safety management

If the initial abnormal behavior cannot be extinguished immediately, subsequently, the massive collateral damage or even fire and explosion may be caused dramatically. As to minimize battery pack damage, guarantee social security, and avoid socioeconomic loss, it is urgent for the BTM to enhance battery safety problem treatment with the combination of emergency cooling, fire extinguish, and thermal barrier. Additionally, the power battery with battery thermo-safety management structure assembly needs the rational and optimized design.

3.3.1 | Emergency cooling

One of the best solutions to extinguish and prevent abnormal operation for battery is to develop an emergency cooling system to reduce the thermal overheating induced by continuous battery temperature rise. The typical innovative design concept of the emergency cooling system is to spray or eject a cooling medium onto the surface of the malfunctioning battery unit to absorb the heat. And thereby, emergency cooling can surely reduce the risk of reaching initiation temperatures of thermal runaway. Additionally, such action is also able to thermally shield off other neighboring battery units in the case of the thermal overheated phenomenon spread of the malfunctioning unit via radiating heat. To maximally enhance the heat transfer ability of the emergency cooling system, phase change medium characterized with nonpoisonous and nonflammable is valuable for popularization and application.^{150,151} Thereby, when the used medium reached to its constant temperature of melting or evaporation, the medium would absorb substantial energy and immediately reduce battery temperature by its evaporation latent.

To stop the evolution of a fire affecting the cells, which is likely to propagate, Cittanova¹⁵² invented a safety device consisted of a gas storage tank containing carbon dioxide CO_2 mixed with nitrogen N_2 and argon Ar , which must be stored in the liquid state. Gustafsson¹⁵³ tested the effect of two different size spray nozzle performances of an emergency cooling spray-on system with a mixture of 25% ammonia (NH_3) and 75% water (H_2O). Then Larsson et al¹⁵⁴ investigated comparison between the HF generation evolution and heat release rate with/without the water mist emergency cooling; schematic illustration of the experimental setup was illustrated in Figure 19. And they also put forward that, when the amount of toxic gas generation of HF and phosphoric fluoride (POF_3) was beyond the normal ranging between 20 to 200 mg/Wh and 15 to 22 mg/Wh, respectively, the water mist began to spray. Thus, the heat release rate and HF production could be delayed when adding a total of 851 g of water in the reaction zone. To lessen the adverse effects of thermal runaway propagation onto adjacent cells, Alex and Arthur¹⁵⁵ provided an active thermal runaway mitigation system, as shown in Figure 20. It is composed of a battery pack enclosure and its emergency cooling conduit with breach points. The fluid storage in cooling conduit can be discharged to battery pack through the breach points as soon as the temperature reached to the melting value. This active thermal runaway mitigation system can link up to an on-board communication system that reported thermal runaway events and operation of the thermal runaway mitigation system to the passengers and an emergency service provider of fire agent. In 2015, Wang and Li¹⁵⁶ used the combination of liquid nitrogen, liquid argon,

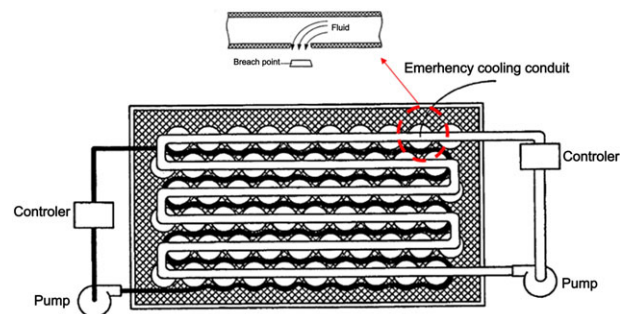


FIGURE 20 The active thermal runaway mitigation system¹⁵⁵ [Colour figure can be viewed at wileyonlinelibrary.com]

and liquid carbon dioxide as spray agent for battery emergency cooling system with determination of the most optimum spraying time for the intermittent and continuous mode. According to this research, the vapor latent amount was defined, which should be 0.1 to 10 times of the thermal runaway heat generation. In 2017, Al-Zareer et al⁷⁷ also proposed a BTMS using liquid propane boiling to remove the heat generated from the battery packs and internal combustion engine, as shown in Figure 21.

Compared with the noble gas of nitrogen, argon, and so on, the refrigerant with a larger evaporation latent undergoing phase changing is much more suitable for early prevention and suppression of the thermal overheated phenomenon. What is more, with the same medium, emergency cooling system interconnected with HVAC refrigerant system can fully facilitate the system simplification and compactness. Although the refrigerant can remove heat relying on the liquid-vapor phase change, care must be taken for refrigerant selection. It should be not reactive with components in the battery,

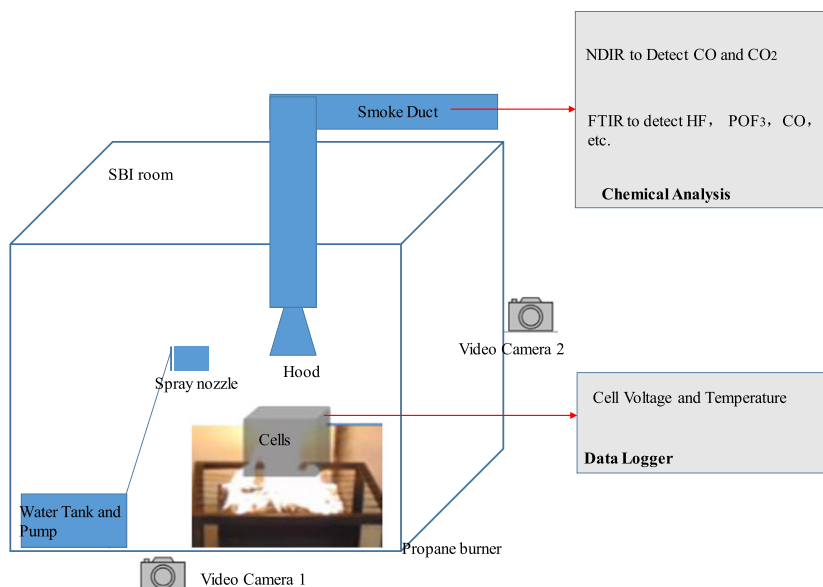


FIGURE 19 Experimental bench of water mist spray¹⁵⁴ [Colour figure can be viewed at wileyonlinelibrary.com]

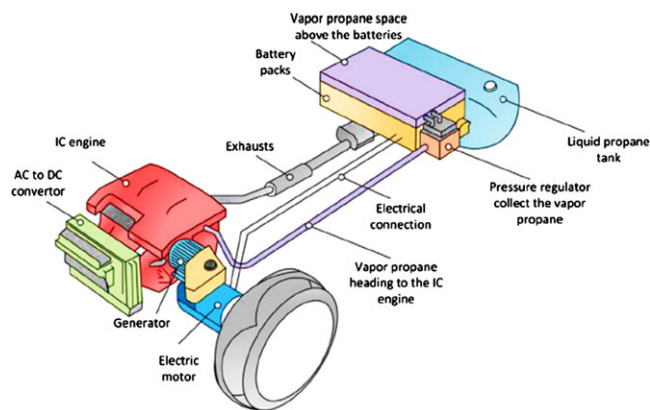
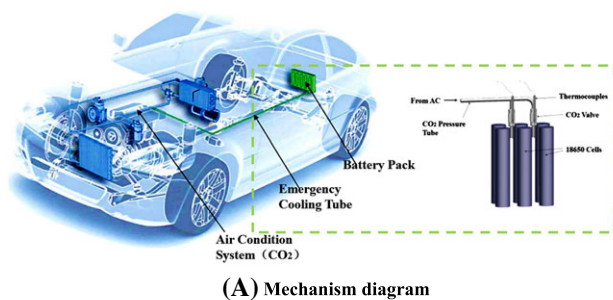


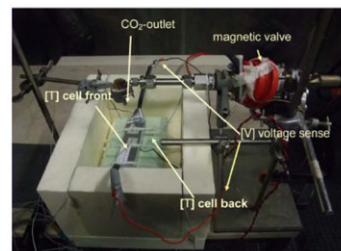
FIGURE 21 Battery thermal management based on liquid propane boiling⁷⁷ [Colour figure can be viewed at wileyonlinelibrary.com]

especially lithium, and should have a large enthalpy of vaporization.

Thus, Bandhauer and Farmer¹⁵⁷ proposed a thermal management system associated with overheated extinguish method that provided enhanced thermal protection via rapid explosive ejection with high pressure refrigerant during abnormal abuse. The adopted refrigerant was R125, whose enthalpy of vaporization was 164 kJ/kg and the saturation temperature at atmospheric pressure was -48.4°C . The additional tank was as heavy as 1 kg for liquid phase R125 storage, so that the cooling power can reach to 2 MW to suppress thermal runaway within 0.1 second. However, it also encountered with some inconveniences of adding weight and volume particularly for a large battery pack system. Consequently, Kritzer et al¹⁵⁸ raised up the concept for the synergetic combination of CO_2 -based MAC systems and hybrid electric vehicle/electric vehicle lithium BTMS, as shown in Figure 22. The mechanism diagram is illustrated in Figure 22A. A special expansion valve is located at the end of the MAC branch conduit, which can control the highly compressed liquid CO_2 to expand throughout the nozzle transformed into gaseous or solid state and rapidly and precisely ejected onto the surfaces of sensed malfunction of the battery and gained a better lightweight. This



(A) Mechanism diagram



(B) Experimental bench

FIGURE 22 Synergetic combination of CO_2 -(MAC) systems and battery thermal management system¹⁵⁸ [Colour figure can be viewed at wileyonlinelibrary.com]

emergency cooling performance can be effective because of the positive Joule-Thomson-Effect coefficient for CO_2 . Then the effectiveness was proven experimentally on a lab experimental bench with the overcharged cell, as shown in Figure 22B. Without the emergency cooling, the cell surface temperature reached to 170°C , and then the cell suddenly ruptured with flying sparks and smoke emission. When temperature reached to 90°C , the emergency cooling cooperated with MAC began to work, and the front surface cell temperature immediately dropped down from 93°C to -49°C within 20 seconds.

3.3.2 | Fire extinguishing

To ensure the safety of lithium batteries during transportation, developing effective fire extinguishing system to reduce a potential risk has become another top priority for BTM and its safety. It should be noted that before the fire spread to a high voltage battery, carbon dioxide or ABC dry powder fire extinguisher can be used. But when flammable electrolyte vapor emission, an effective attempt is to cool the battery with the massive water of high pressure continually.

Seung-hun et al¹⁵⁹ disclosed a fire detection sensor for detecting the probability of fire occurrence at a battery pack, a fire-extinguishing chemical tank, and a control unit allowing for the fire-extinguishing chemical injected into the battery pack to suppress fire at an early stage. Kim and Yoon¹⁶⁰ delivered a safety device for spraying a material to restrain the fire or the explosion of the battery pack. Engineers from VOLVO provided a battery coated with a fire-extinguishing function, which included a fire-extinguishing tank storing compressed air and fire-extinguishing fluid. Therefore, the fire-extinguishing tank busted, and the fire-extinguishing fluid contained in the tank can be sprayed to the battery. On the basis of the independent built burning and explosion experimental platform installed with a combustible gas detector, Qi et al¹⁶¹ provided a better understanding of suppressing performance with water mist for a burning lithium-ion battery. The simulation of the experimental result is

provided in Figure 23. The extinguishing efficiency of the water mist with different droplets diameter and the spray speed, intensity, and angle were totally discussed. It was proposed that, on the premise of ensuring extinguishing efficiency and reducing economic cost, the optimum solution of BTM enhanced its safety was to install a single nozzle with the spraying direction of vertically downward, 100 μm droplets diameter, 30 m/s spray speed, 2 L/min spray intensity, and 60° spray angle.

3.3.3 | Thermal barrier

When a battery undergoes thermal runaway, it typically emits a large quantity of smoke, flammable vapor electrolyte, and massive heat resulting in the combustion and destruction of materials. One approach to overcome this problem is to reduce the risk with thermal barrier with high resistance, that is, to promote the passive security.

Thus, Mehta et al¹⁶² provided a means for inhibiting the propagation of thermal runaway composed of battery cells coated with a layer of intumescent material. Their simulation results illustrated that the intumescent material can absorb thermal energy to delay the thermal runaway onset temperature for the adjacent cells. And this function was then verified by Hu et al.¹⁶³ Figure 24 is the sandwiched structure of battery cell, heat conduction layer, and the heat insulation layer. And the simulation results showed that, with an aluminum material heat conduction layer of 0.1 cm thickness and the heat insulation layer of 0.2 W/(m·K) thermal conductivity coefficient, the safety of the entire battery module can be definitely ensured.

Referring to the low thermal conductivity and heat absorbing property, the phase change material can be used to insulate the thermal runaway diffusion inside the battery. Kizilel et al¹⁶⁴ investigated the passive cooling with Phase Change Material (PCM) contribution in

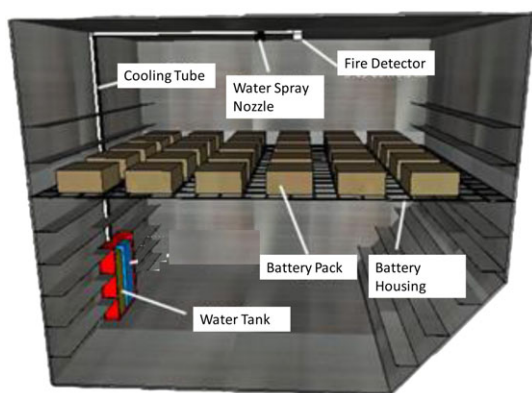


FIGURE 23 Simulation results with different the droplets diameter and of the spray speed, intensity, and angle¹⁶¹ [Colour figure can be viewed at wileyonlinelibrary.com]

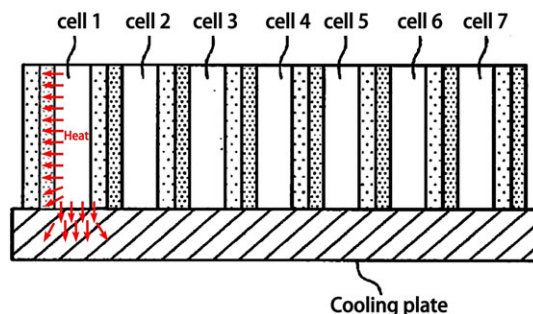


FIGURE 24 The protection structure¹⁶³ [Colour figure can be viewed at wileyonlinelibrary.com]

preventing the propagation of thermal runaway. Compared with runaway propagation of air cooling, owing to the PCM-graphite matrix advantages in absorbing and spreading the heat very quickly, the runaway did not propagate and module average temperature returned to ambient values of 25°C in 40 seconds. Wilke et al¹⁶⁵ then verified it when the space between the cells equaled to 2 mm, with the phase change composite materials plate, the thermal overheated temperature of the triggered cell can be reduced from 198°C to 109°C; additionally, the neighboring cells temperature can be decreased by 60°C or more. It elucidated that the propagation consequences can be alleviated from the aspects including not only individual cell but also battery pack scale.

To realize a much more long-life span power battery system with intellectualization and thermo-safety, the thermo-safety prevention and control mechanism of the thermal safety management should be strengthened from different multiscaled levels. It should be noted that the active method should be collaborated with passive thermal safety management design. So the requirements of absorbing the heat and reducing the risk of thermal runaway can be fully achieved.

4 | FUTURE TASK AND PROPOSAL

As noted previously, with the rapid development of electric vehicles, power batteries applications are heading into large capacity, high specific energy density, and fast charging and wide temperature range. Thus, battery suffers from safety problems due to an increase in the heat generation rate and life span aging and degradation acceleration, meanwhile, the deterioration of stability. Thus, the technology of BTM with its enhanced safety has already been an important research hotspot. As to enhance and improve battery safety, there are usually two main ways. One is concerning to battery material modification. For example, to improve electronic conductivity and lithium-ion diffusion rate for the material of

solid electrodes, electrolyte and SEI. This method of material modification can be beneficial for battery thermal stability capability and cycling performance. The other one is to strengthen the BTM to maintain its safety and efficiency during the whole operational process. And the latter can be realized through the technology of BTMS and its enhanced safety.

First of all, electrical vehicle thermal management should not only ensure the optimal working condition via cooling and heating methods but also have the ability to cope with the battery overheating and even thermal runaway under various abusive conditions. To strengthen battery thermal safety, it should adopt the active design of the emergency cooling and fire extinguishing and the passive thermal barrier design. This method of BTM with its enhanced safety can surely absorb the heat and reduce the risk of reaching initiation temperature of thermal runaway. It should be noted that in the event of overheating or even thermal runaway, it can thermally shield the heat to adjacent cells. The BTMS has been constantly learning and adopting the heat transfer enhancement cooling methods. Such as hydronic circulation cooling, cooling method coupling with HVAC, and the refrigerant direct cooling method. Concerning to the direct cooling with refrigerant, it has a better potential for safety improvement owing to its large evaporative latent heat and the quick response for its compacter structure. And it also can be extended to refrigerant spraying and ejection of thermal safety emergency cooling to block the oxygen and inhibition battery combustion.

Furthermore, to satisfy the sustainable development needs of green-energy vehicles, the proposal can guide the energy conservation and efficiency, and the work outlook for R&D of BTMS with enhanced safety should concentrate on thermo-fluid parameter and its cooling pattern optimization, battery thermo-electrical-chemical characteristics during normal/abnormal operation, battery multiple signal detection and identification, and the ability to predict and control the overheating propagation and fire spread. Meanwhile, the attention should be paid on the BTMS controlling rule, functional mechanism, and diagnosing/predicting performance. To realize a much more long-life span power battery system with intellectualization and thermo-safety, the major matters of relevant core issue involved the following:

- 1 The heat transfer enhancement and thermo-safety prevention and control mechanism of the refrigerant direct cooling should be strengthened from different multiscaled levels.
- 2 An accurate diagnostic analysis system with real-time monitoring of the thermal behavior and safety status during the battery overall operating states is required

to judge the battery damage, aging, and module degeneration and to warn when the presetting abnormal threshold has been exceeded.

- 3 The refrigerant direct cooling method can be applied to battery thermal safety synergy control for its potential in emergency cooling of spaying and prevention overheating or thermal runaway propagation.
- 4 The optimize design of integrated vehicle synergy control mechanism and its mode switch should be built up, which uses the BMS and BTMS based on refrigerant direct cooling method or other cooling methods coupling with HVAC.

Additionally, after reviewing relevant research and key technology of BTM with its enhanced safety, it can be concluded that the integrated vehicle synergy mechanism and its state real-time predictability and controllability are expected to be researched, developed, and solved. And an innovation and prospective research is to improve the technical capacity of BTMS with its safety enhancement. There exist commonality and individuality issues in this field requiring further investigations, just summarized as follows:

- 1 Analysis and cognition of the power battery with battery thermo-safety management structure assembly should be enhanced. And the rational design and its structure parameter need to be optimized.
- 2 The performance of BTM with its enhanced safety including its heat and mass transferring and battery thermal controlling laws should be figured out under various operational conditions. That may include system architecture, flow pattern, battery configuration, heat transfer scale, flow distribution, warm section configuration, dynamic load, electrochemical heat, Joule heat, load stacking, vehicle behavior, climate conditions, etc.
- 3 The battery pack model to describe battery thermo-electrical-chemical behavior needs to be established. It can timely reflect a large group of multiheat sources temperature timely variation and the heat generation/transferring transient process.
- 4 The BTM with its safety enhancement should switch its cooling mode according to the different demands; that is to say, the thermal/electrical/biochemical thresholds should be set in advance. Through the effective monitoring system, the dynamic prediction and diagnose can be realized.
- 5 The method to define the safety status of a battery is critical for battery thermal safety management. It decides the triggering timing to perform the active implement of emergency cooling and fire extinguish. And also, to build an analysis numerical model can

- be conducive to investigate this cross-coupling problem.
- 6 The BTM with its safety enhancement involves many aspects such as refrigerant cooling under ultra-low temperature, emergency cooling, and fire prevention. The rules of controlling performance, thermopneumatic characteristics, and pressure/temperature field variations should be summarized up.
 - 7 As another aspect of BTM with its safety enhancement, refrigerant spraying of emergency cooling can absolutely achieve temperature drop suddenly for its large evaporative latent. And it is also beneficial to dispel toxic gas produced along with battery secondary reactions. So its jet stream flow pattern and course including the angles, mass flow, and inlet temperature should be further discussed.
 - 8 To enhance battery pack thermal safety, battery management system should cooperate with BTMS. Their cross-coupling controller strategy should be optimized with feedforward and feedback synergy control.
 - 9 The BTM with its safety enhancement is always performed in collaboration with battery cooling system, HVAC system, thermal safety management system, etc. The operational performance design, analysis, and prediction of different equipment and their accessories should be investigated through experimental bench or multiple systems modeling of the integrated electrical vehicle.

At last, the systematical research, fundamental approach, and prospective investigation are urgent to be strengthened for the issues discussed above. A full cognition of BTM with its safety enhancement should be set up for the technological innovation and application mechanism to accelerate BTM technology advancement and realize battery thermal safety technology leapfrogging. Actually, the listed problem, future work task, and proposal synthesize the science of BTM and its enhanced safety and also provide a solid foundation for a better understanding of these key issues. With this guidance and exploratory study, it has the important theoretical value and practical significance for perfect theory and engineering application. There is no doubt that it can strongly facilitate the technology of BTM and its enhanced safety to develop sustainably.

5 | CONCLUSION

On the basis of the battery behavior analysis of the overall process from heat generated to overheated, BTM with enhanced safety can satisfy the requirements including the guaranteed battery performance with cooling/

preheating, the reorganization of overheated status, and sending alerts signals before the thermal runaway onset time via various advanced measurements. Additionally, it can inhibit battery thermal overheating at the individual cell level and take precautions against the potential for cell to cell propagation through the combination treatments adopted in BTM and its safe enhancement of emergency cooling, flame extinguishing, and thermal barrier.

It is concluded that the BTM enhanced safety could have a three-layer design concept. Firstly, it can ensure battery operation under optimal temperature range. Secondly, it can detect the critical point of battery failure and deliver alarm messages. Finally, as soon as the thermal hazard happened, the treatment can suppress thermal runaway propagation effectively. Featured with multilevel, multifunctional, and multiinteraction, it can be inferred that the relevant research status and key technology of BTMS with enhanced safety has been promising for the sustainable development needs of the long-term mechanism of energy conservation and green-energy vehicles marketization.

This article provides a comprehensive review on BTM with enhanced safety and aims to promote the battery application of high energy density, security, and cyclic stability served for electrification and intelligentization of automobiles.

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NOMENCLATURE

A	preexponential factor of the reaction, s^{-1}
c	dimensionless variables interpreted the fraction of the remaining reactant
$\frac{d}{dt}$	the derivative of variable
E	activation energy of the reaction, J/mol
h	enthalpy of each reaction, J/kg
m	reaction order parameters
M	mass of reactants, kg
n	reaction order parameters
P	static pressure, Pa

q_G	system heat release rate, W
q_L	system heat dissipation rate, W
\dot{q}	heat generation, W
Q	thermal energy, kJ
R	universal gas constant of 8.314, J/(mol·K)
S	superficial area, m ²
soc	state of charge, %
t	dimensionless variables of thickness
T	temperature, K
T_0	environmental temperature, K
U	surface coefficient of heat transfer, W/(m ² ·K)
W	density of reactants, kg/m ³
y	fraction of vented electrolyte
ΔH	specific heat released, J/kg
θ_e	fraction of electrolyte in liquid phase
χ	fraction of Li in the electrodes

SUBSCRIPTS

boil	denotes the variable for the boiling of the electrolyte
e	denotes the variable for electrolyte decomposition reaction
ej	denotes the variable for the electrolyte venting of the eject
electrode	denotes the variable for electrode reaction
ne	denotes the variable for cathode reaction with electrolyte
pe	denotes the variable for anode reaction with electrolyte
sei	denotes the variable for SEI decomposition reaction
vent	denotes the variable for venting of the electrolyte

ORCID

Yan Wang  <http://orcid.org/0000-0001-8329-1349>

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