Research progress on efficient thermal management system for electric vehicle batteries based on two-phase transformation

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Abstract

Given the energy situation and the rapid growth of the electric vehicle market, electric vehicles (EVs) will face high battery heat production and performance issues brought about by increased range and fast charging performance. Battery thermal management systems (BTMS) for EVs must provide higher heat transfer efficiency to ensure proper battery operating temperature with higher energy density and lower energy consumption to improve current vehicles. The two-phase transformation involves the absorption and release of latent heat from the working medium to achieve efficient heat transfer, and the related heat transfer technology is considered to be an effective approach to the current iterative upgrade of BTMS. This review classifies the existing concepts of thermal management for EVs based on phase change technology and reviews the development of each technology to comprehensively analyze the advantages and disadvantages of the studied technologies. Finally, the opportunities and challenges for technology development are summarized, and recommendations are provided for future research to advance the commercialization of EV phase change technology.

Keywords: Battery thermal management systems; Electric vehicle; Lithium-ion batteries; Phase change technique.

Nomenclature	
T_{max}	Maximum temperature of the battery pack
$\triangle T$	Temperature difference of battery pack
Q	Cooling capacity
$\dot{m}$	MMass flow rate
ρ	Density
ΔP	Pressure drop
η_L	Volume criteria of the batter pack
η_m	Mass criteria of the batter pack
L	Height of the battery pack
m	Weight of battery pack
Subscripts	
mc	Maximum capillary
v	Vapor
l	Liquid
g	Gravity
ave	Average
Acronyms	
EV	Electric vehicle
HEV	Hybrid electric vehicle
ICE	Internal combustion engine
BTMS	Battery thermal management system
DOD	Depth of discharge
SEI	Solid electrolyte interface
AC	Air conditioning
ODP	Ozone depletion potential
CPI	Cooling performance index
GWP	Global warming potential
PCM	Phase change material
PA	Paraffin

TME	Trimethylolethane
EG	Expanded graphite
AlN	Aluminum nitride
ER	Epoxy resin
LDPE	Low density polyethylene
OBC	Olefin block copolymer
SBS	Styrene butadiene styrene
TPE	Thermoplastic elastomer
POE	Polyolefin elastomer
NR	Natural rubber latex
CMC	Carboxymethyl cellulose
SAT	Sodium acetate trihydrate
STP	Sodium thiosulfate pentahydrate
HCs	Hydrocarbons
HFCs	Hydrofluorocarbons
HFOs	Hydrofluoroolefins

1. introduction

The energy crisis and growing environmental problems have prompted countries around the world to pay attention to carbon emissions and begin to develop strategies to reduce carbon emissions and achieve carbon neutrality. Driven by government policies, industries are beginning to electrify while accelerating the application of electrochemical energy storage, especially in the transportation field. Electric vehicles(EVs) or hybrid electric vehicles(HEVs), by using battery packs as the energy storage as well as the primary energy supply element, have been considered as a green alternative to traditional fuel vehicles, which is supported by the results of the life cycle analysis (LCA) assessment of EVs[1]. In 2010, the Electric Vehicle Initiative

(EVI) was established under the Clean Energy Ministerial(CEM), a multi-governmental policy forum that has been working to accelerate the adoption of EVs globally. So far several governments have taken a variety of measures to help the popularity of EVs, including subsidies for the purchase of EVs[2], infrastructure for charging facilities[3], and enhanced incentives for the battery industry. Several car manufacturers including Toyota, Ford and Volvo plan to accelerate the goal of fully electrified vehicles through new product lines. The current EV market is expanding rapidly, with EV sales in 2021 already doubling from the year before and continuing to rise strongly in the future[4].

However, EVs or HEVs are still not fully comparable to internal combustion engine (ICE) vehicles in terms of usability, including longevity, limited all-electric range, fast charging and safety, which is closely related to the important component of EVs, the battery pack. The lithium-ion batteries mainly utilized in EVs possess high energy density and low self-discharge rate, but have high sensitivity to temperature. Therefore, for lithium-ion batteries, which generate heat during charging and discharging, EVs usually provide thermal management systems to monitor battery health and control the operating temperature of lithium-ion batteries in the appropriate range to maintain the performance, life and safety of the battery pack[5-9]. Conventional battery thermal management systems(BTMS), which are also commercially adopted for EV thermal management solutions, can be divided into air cooling [10, 11] and liquid cooling[12, 13] according to the cooling medium, and have been discussed in detail in several reviews mentioned above. The air-cooled

BTMS is simple in structure and has a low cost, but limited by the lower convective heat transfer coefficient of air, this type of BTMS provides insufficient cooling conditions for the high energy density lithium batteries used in EVs[14], and the same problem is reflected in the high rate charge/discharge conditions[15]. Liquid-cooled BTMSs offer the advantage of temperature control over air-cooled BTMSs by providing higher cooling efficiency and cooling capacity, and lower system power consumption at high discharge conditions of the battery[16, 17]. However, the disadvantage of such a system type is the complexity of the required fluid channel connections and configuration, which increases the possibility of errors and the risk of fluid leakage[18]. With the demand for fast charging and high range, lithium-ion batteries need to go to high energy density, accompanied by high heat production of the battery, which requires a greater cooling capacity of BTMS[19]. As the battery capacity and charge/discharge rate increase, it is difficult for liquid-cooled BTMS to meet the battery temperature control requirements for operating conditions[20]. Therefore, the thermal management system of EVs needs to be updated with more efficient heat transfer technology.

The process of transition between vapor-liquid-solid phase states absorbs or releases latent heat, and has a significantly higher heat transfer efficiency than single-phase heat conduction and convection. Based on this principle, the corresponding phase transition heat technology has been developed and implemented for specific applications, including data centers, electronic devices and other areas. Therefore, the heat transfer technology of phase change has started to be developed in the field of EV battery thermal management, mainly including two-phase coolant cooling, phase change materials(PCMs) cooling and heat pipe cooling. Some of the reviews discuss the features and development of the techniques individually, including heat pipe cooling[21-23], PCM cooling [24-26], and hybrid BTMS[27], but lack the details and correlations of the other phase change techniques. And some comprehensive reviews have explored the three technologies[28-30], it is more as an extension of the traditional BTMS or an integral comparison. The differences in the implementation solutions of each technology and the connection to the development requirements of BTMS for EV are also ignored in the comparisons and discussions. Therefore, the present work classifies the three mentioned two-phase thermal technologies according to the developments and outlines the principles of each technological solution. Subsequently, the progress and characteristics of the technology development are summarized by reviewing the current status of research in recent years. Further, the development direction of the technologies is analyzed and predicted based on the battery thermal requirements, aiming to promote the introduction of phase change technology into the EV thermal management market.

2. Thermal characteristics and requirements of EV power batteries

2.1 Lithium-ion battery heat generation principle

A lithium-ion battery contains a multi-layer cell with current collectors, an anode and a cathode inside the cell, and between the electrodes is an electrolyte for ions transfer and a separator to prevent the effects of internal electron transfer[31]. The storage and discharge capacity of the battery comes from the diffusive transfer of Li^+

and the electrochemical reaction with the electrode, and the working mechanism of the cell in the normal state is shown in Fig. 1(a). Fig. 1(b) reflects the heat generation of each component in the cell. The electrodes contribute the major heat production in normal operation, but charging and discharging are reflected in different electrodes[32]. This heat is also the result of the superposition of multiple internal heat generation mechanisms, part of which comes from the entropic heat production of the intercalation /deintercalation process of Li^+ at the electrode. The other type of heat is considered to be irreversible and is generated by the deviation of the electrode potential from the equilibrium potential, namely the polarization phenomenon. Polarization phenomena are classified as activation polarization, diffusion polarization, and ohmic polarization. The ohmic polarization is caused by the resistance of the material and electrolyte to electron transport and ion transport, and its heat production is known as the ohmic heat, while the heat production of the rest of the polarization phenomena is known as the polarization heat[33, 34]. In general, a large portion of the heat production of the battery is irreversible heat and is related to the SOC of the battery, as shown in Fig. 1(c). And the polarization heat is the dominant heat generation at an operating temperature greater than 5°C[35, 36]. Alternatively, the heat generation rate in the electrode plane is determined by the current density and varies with the current density distribution at different SOC conditions, as shown in Fig. 1(d)[37]. In addition, heat is generated when the current passes through the current collector, collecting tab and other components, which is especially significant in high C-rate operating conditions[38, 39].

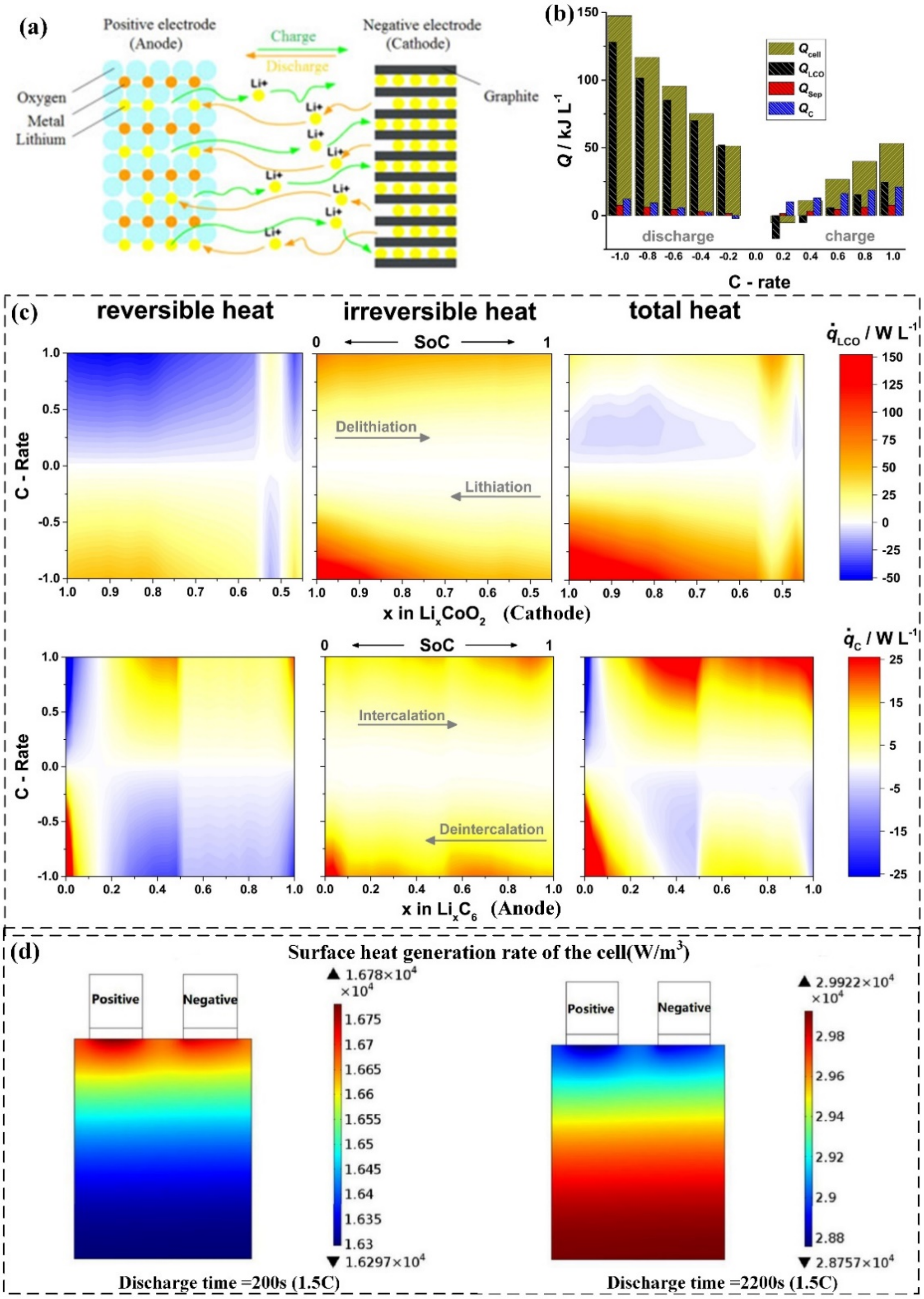

Fig.1. Mechanism and heat distribution inside lithium-ion battery: (a) Charge and discharge mechanism in the cell[31]; (b) Heat generation of cell components[32]; (c) Heat generation rate of the electrode[32]; (d) Heat generation rate distribution of the cell surface[37].

In summary, the heat production of lithium-ion batteries has multiple mechanisms of compounding and presenting different magnitudes in each component, showing a kind of non-uniform heat production rate distribution in general. Meanwhile, the heat transfer inside the cell is affected by the difference in material properties and the thermal resistance of each layer contact. The electrodes in a single cell are determined by the thermal conductivity of the electrolyte and active particles, the current collector has a high thermal conductivity as a metallic material, while the separator is extremely low because of the microporous polymeric nature[40]. This also makes the thermal conductivity of the battery anisotropic, leading to temperature inhomogeneity inside the battery[41]. Several reviews have also summarized the mechanistic studies of battery heat generation[42] and battery-related modeling[43].

2.2 The potential hazards of lithium-ion battery

Lithium-ion batteries are mainly divided into cylindrical batteries, prismatic batteries and pouch batteries according to the form of the packaging, all of which are composed of multiple cell laminations and share a common heat production principle. Cylindrical and prismatic battery shells are made of aluminum alloy, stainless steel and other materials, which are hard shell packaging, while pouch batteries are made of aluminum-plastic film, which is lighter in weight and more flexible in design than the same capacity battery, but less protective performance. Nevertheless, the pouch battery is more consistent with the trend of high energy density of the system, but still needs to be improved in manufacturing and battery grouping.

According to the occurrence temperature of various reactions in the lithium-ion battery, the most suitable temperature of the battery is 15-35°C[44]. When the battery is out of the normal operating temperature range, a series of side reactions will be induced inside the battery to lead to thermal runaway. Low-temperature conditions may induce lithium deposition, plating and dendrite at the electrode, which may trigger some reactions with electrolyte and self-heating phenomenon, and may also break through the diaphragm leading to an internal short circuit[45]. Fig 2(a) and (b) show the reactions and specific reaction processes triggered by different temperatures inside the battery. As the battery temperature rises, the high temperature will trigger the decomposition of the solid electrolyte interface (SEI), the melting of the separator, the decomposition of the electrode material and the electrolyte side reactions[46, 47]. These processes are accompanied by different types of exotherms and may proceed in chains, and are more likely to occur at high charge and discharge rates[48]. This is considered as a negative factor that reduces the thermal safety of the battery.

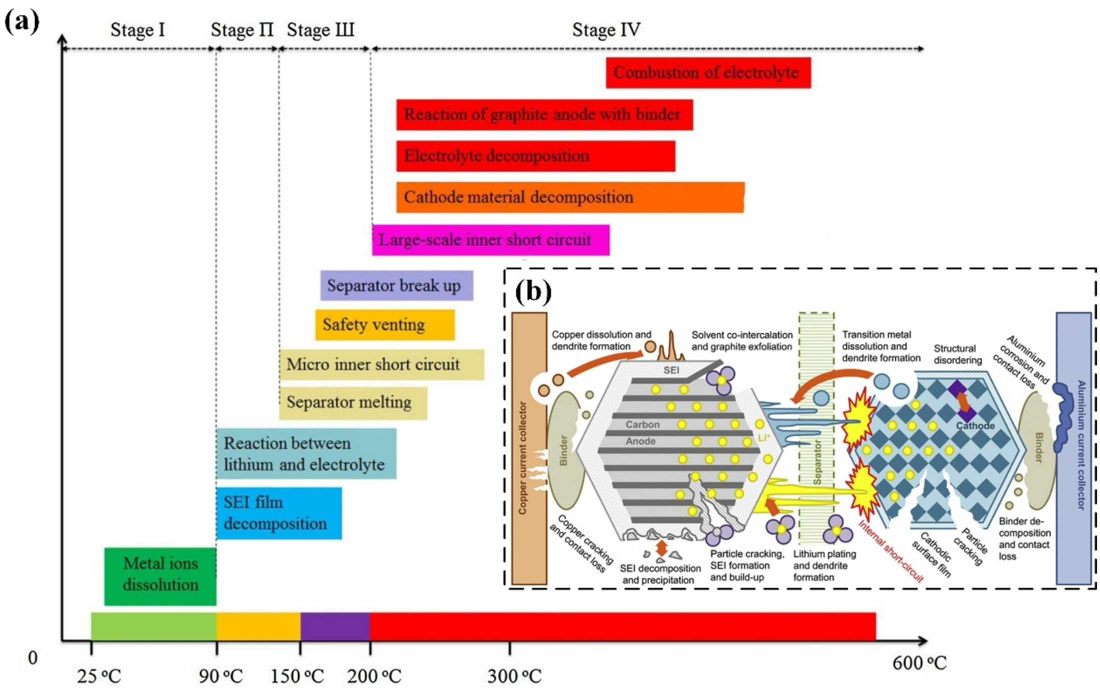

Fig.2. Heat generation process inside the lithium-ion battery: (a) Exothermic reactions inside the battery at different temperatures[46]; (b) The side-reaction process of the battery caused by the temperature rise[47].

Besides the temperature of the battery, the pressure on the surface is also a factor that affects the performance of the battery. During the charging and discharging process, the battery experiences expansion, mainly caused by the formation of SEI and the volume change of the anode and cathode layers[49, 50]. When under high temperature or high charge/discharge conditions, the battery expands more significantly in the thickness direction[51], while exhibiting a linear expansion behavior under unconstrained conditions[52]. Batteries grouped in EVs are usually fastened by rigid components with mechanical restraint to ensure the compactness of the system, which also inevitably exerts a certain compression force on the battery. Related studies have shown that stress evolution has a significant effect on the battery capacity decay characteristics. Smaller stresses prevent cell layer delamination and help the battery maintain long-term performance, but when the stress is higher, the battery shows a faster capacity decay rate[53-55]. This is mainly reflected in pouch batteries with weaker mechanical properties.

2.3 Development of BTMS for EVs

Based on the above factors affecting battery performanceand considering the complexity of environmental conditions faced by EVs, the current BTMS sets the maximum allowable temperature range of the battery pack at 25-50°C, in which the side reactions have less impact on the battery performance[56]. In addition, differences in the individual batteries in the battery pack can also trigger negative effects such as battery capacity decay and accelerated battery aging, while the direct factor is the temperature difference of the battery[57-59]. Therefore, the temperature difference between batteries should be less than 5°C, which is also an essential index for the performance assessment of the BTMS. Apart from meeting the basic thermal control requirements of the battery, EVs still require a BTMS with high energy density, that is, to ensure good mechanical performance while minimizing the complexity of system components, weight and operating energy consumption.

With the demand for EV development, fast-charging technology has to be improved gradually. Current fast charging technology takes 30min to charge the battery from 20% state of charge (SOC) to 80% (peak charge rate of 3C), while the extreme fast charging will compress that time to 1/3, meaning the peak charge rate will reach 6C or more[60]. As a result, the BTMS needs to improve the ability and efficiency of heat dissipation to ensure that the battery is within the temperature control threshold[61]. Therefore, more efficient phase-change heat transfer technologies have been adopted for the BTMS of EVs. The two main categories of phase change processes applied in BTMS are evaporation/boiling and condensation, melting and solidification processes, which can form the classification shown in Fig. 3. The technologies based on evaporation/boiling and condensation are two-phase coolant cooling and heat pipe cooling, respectively. Different coolants are now available for battery heat dissipation through a variety of cooling methods, while various structural types of heat pipes are also involved in the study of BTMS. The application of melting and solidification processes is mainly reflected in PCM, and several material types of PCM are also involved in the discussion of the study. For heat pipe and PCM will still combine some cooling methods to complete the design of

BTMS. Further coupling of the two phase-change technologies is also derived to obtain a more comprehensive BTMS performance.

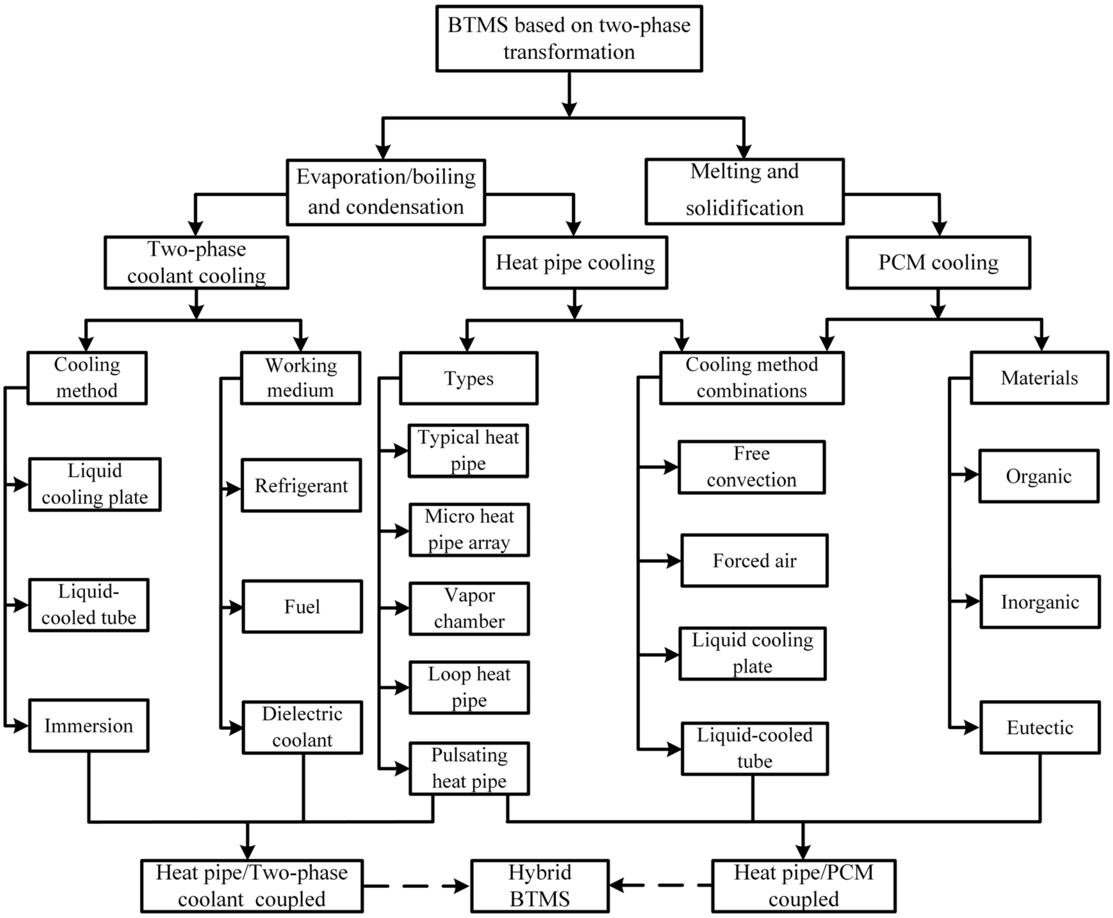

Fig.3 Classification of phase-change technology solutions applied to BTMSs

3. BTMS based on two-phase coolant cooling

The principle of two-phase coolant cooling is based on the use of latent heat from the boiling of the coolant to absorb the heat produced by the batteries and relies on two-phase flow to enhance convective heat transfer. Although similar to single-phase liquid cooling strategies, employing a liquid working medium as the primary heat dissipation medium for heat exchange with the battery, it is more efficient in terms of heat transfer capability. The technical approach is consistent with liquid cooling is divided into two main categories: one is indirect cooling with cold plates and tubes as coolant flow channels; the other is immersion cooling with direct contact between the coolant and the battery, as shown in Fig. 4. The former belongs to forced convective boiling in the tube that needs to be maintained by external pressure difference, while the latter belongs to pool boiling with fluid movement caused by temperature difference and bubble disturbance[18]. To achieve an effective boiling heat exchange, the choice of coolant requires a boiling point within the operating temperature range of the battery and includes medium already used in EV or HEV systems, such as refrigerants and fuels, but also includes dielectric coolants.

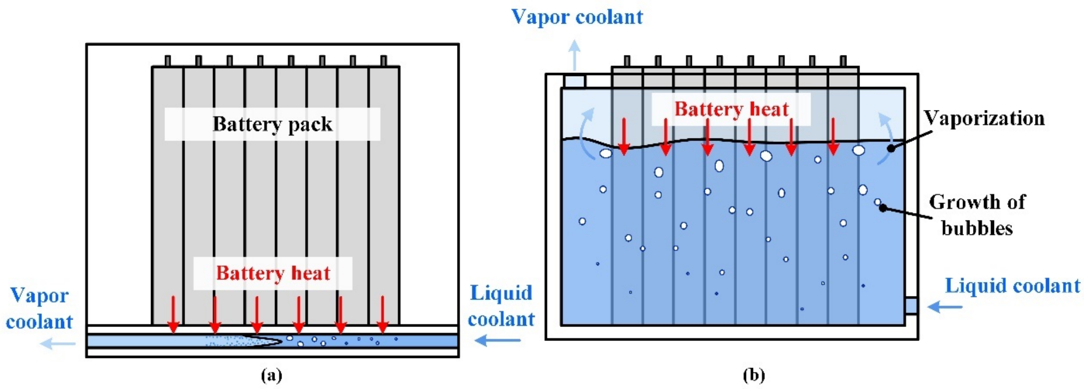

Fig. 4 Schematic diagram of two-phase coolant cooling battery: (a) Indirect cooling by cold plate and cold tube; (b) Direct cooling by immersion.

3.1 Refrigerant

The system of refrigerant cooling is to integrate the air conditioning cycle of EV with the battery pack cooling module, and the air conditioning(AC) system provides the cooling medium for thermal management. A basic structure of the system is shown in Fig. 5. The advantage of such a system design is there is no need to add additional equipment such as condensers and heat exchangers, thus reducing the system weight[62]. This cooling system has been adopted in some models, including the BMW i3, X5 PHEV, Mercedes-Benz S400 Hybrid and BYD Dolphin, and mainly use indirect cooling based on microchannel cold plates in the battery pack.

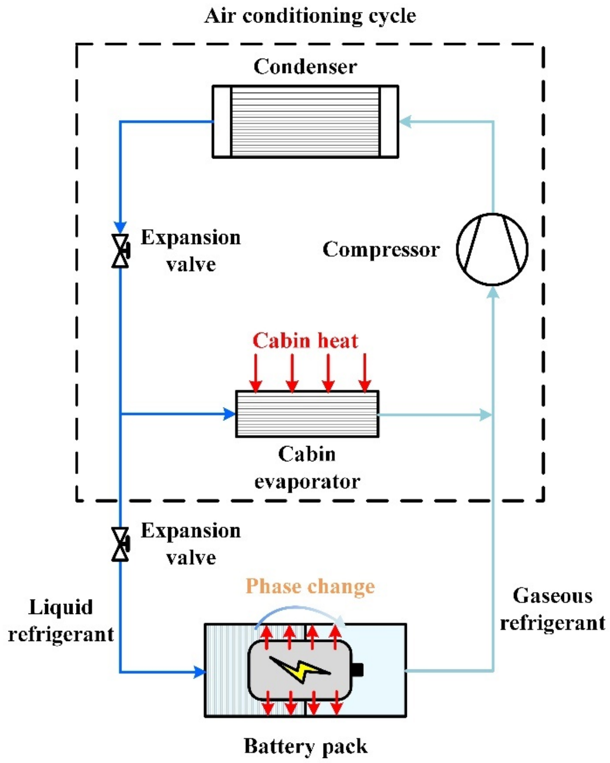

Fig. 5 Schematic diagram of refrigerant cooling system

R134a is commonly used as a refrigerant in passenger car air conditioning systems because of high safety, good thermophysical properties, and the zero-ozone depletion potential (ODP). Cen et al.[63] designed a special aluminum frame for the 18650 cylindrical battery pack, which is designed to allow close contact between the modules, while finned serpentine tubes are arranged between the packs as flow channels for R134a refrigerant. The experiments were conducted at a high temperature of 40°C. It can be seen that the design of the refrigerant circuit has a large effect on the temperature difference $\triangle T$, and a proper circuit design can reduce the temperature difference of the battery pack by 6°C. Wang et al.[64] designed a system based on two-phase cooling by cold plate and developed an electro-thermal coupling model considering the current distribution of the battery and the phase change process of the refrigerant in the microchannel. By analyzing the effects of initial refrigerant temperature, flow rate, saturation temperature, thermal conductivity and latent heat of the refrigerant on the battery, it can be found that the change of initial temperature or inlet flow rate can significantly adjust the maximum temperature of the battery. Shen et al.[65]proposed a more comprehensive analysis criterion for structural optimization. The criteria mainly include: thermal characteristics, cooling performance index(CPI), volume and mass, and welding treatment method.

$$\text{CPI}=\frac{Q\rho}{\dot{m}\Delta P} \tag{1}$$

$$\eta_{\text{L}}=\frac{L-L_{ref}}{L_{ref}} \tag{2}$$

$$\eta_m=\frac{m-m_{ref}}{m_{ref}} \tag{3}$$

where Q is the cooling capacity, $\dot{m}$, ρ and ΔP are the flow rate, average density and pressure drop of the refrigerant, respectively. L_{ref} and L are the battery pack heights before and after the thermal management system is installed, respectively. m is the total weight of the battery system, and m_{ref} is the weight of the batteries.

The evaluation based on the criterion can determine an optimal liquid-cooled plate channel size, but the structural optimization of the liquid-cooled plate produces a much lower improvement in cooling effect than the increase in pressure drop. R1233zd is also used as a refrigerant in thermal management systems. Fang et al.[66] analyzed the thermodynamic cycling of such systems and the thermal performance parameters of the components under steady-state conditions, and also explored the effect of the transient response of pump-controlled systems. The study illustrates that the refrigerant flow rate in the system is not affected by the variation of vapor pressure, while the effect of the flow rate on the heat transfer effect is related to the heat load provided by the battery. The cold plate temperature in the system can be effectively reduced by pump-on control when the heat load increases in vain. To evaluate the applicability of refrigerant cooling, Hong et al [67]compared the thermal performance of two-phase refrigerant cooling with conventional liquid cooling of the same profile through full-scale tests under actual vehicle conditions. The module structure is presented in Fig.6(a). Because of its compactness and fewer channels, the cooling module weighed 56% less than the liquid-cooled module, while the battery capacity under refrigerant cooling is 16.1% higher and the internal resistance is 15.0% lower compared to liquid cooling.

Although the thermal management system of two-phase refrigerant cooling is more simplified, the whole system should be designed to meet the needs of both cabin and battery pack, i.e. to achieve different target temperatures for cabin air and battery pack, due to the merger with the EV air conditioning system. The difference in heat transfer coefficients between the internal evaporator and the cooling plate also imposes the requirement that the refrigerant temperature in the internal evaporator should be lower than the temperature in the cooling plate, which is also a certain conflict in the application strategy. Therefore, it becomes especially important to solve the problems on both systems effectively. Shen et al.[68] built a system with two layouts of the refrigerant cooling system in series and parallel connections based on an EV simulation model including cabin, battery and air conditioning sub-models.

The comparison revealed that there was no significant difference in the battery cooling effect and optimal refrigerant charge for both connection forms, but the exergy efficiency and COP were higher for the series-connected system than for the parallel-connected system. Further, the effects of driving conditions, ambient temperature and air conditioning operation mode are analyzed, where driving conditions are characterized by the volumetric efficiency, isentropic efficiency and mechanical efficiency of the compressor. In the study, the average temperature of the battery can be maintained at 25°C regardless of the high temperature or the high speed conditions of the EV, while the temperature difference is kept at about 3°C[69]. Wang et al.[70] added an electronic expansion valve (EXV) behind the battery cooling/heating plate in the refrigerant branch to balance the heat distribution between the cabin and the battery. By adjusting the EXV opening the refrigerant dryness at the cooling plate outlet can be reduced, which helps to improve the temperature uniformity, but also reduces the system COP accordingly. Ataur et al.[71] propose a refrigerant cooling BTMS with fuzzy control, where the battery temperature is measured by sensors and controlled by fuzzy control of the electric compressor and expansion valve as a response. The experimental results revealed that the system can keep the battery temperature within a safe range of 25~40℃ and save at least 17.69% energy compared to the air-cooled battery thermal management system. Guo et al.[72] proposed a BTMS that enables cooling and heating of the battery by the refrigerant, so that the battery preheating does not require a PTC heater or an additional coolant circuit. It also uses a control strategy that independently controls the evaporation temperature of the internal evaporator of the battery pack and cabin air. The results show that the battery temperature can be controlled in the set value range in both summer (35 ℃) and winter (0 ℃).

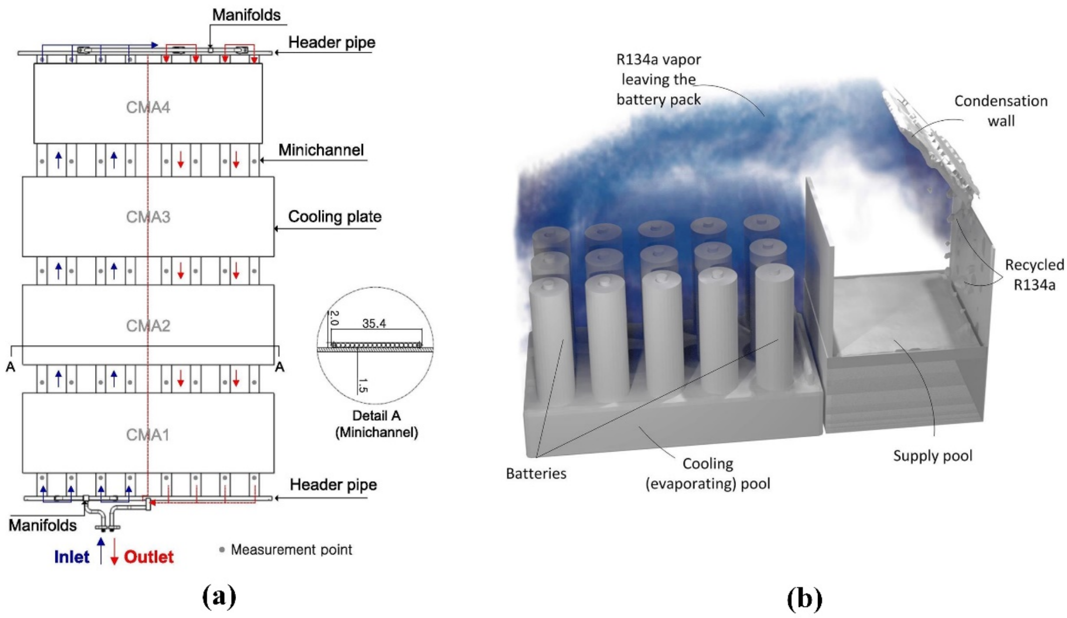

Fig. 6 Refrigerant cooling system: (a)Cooling module based on the cooling plate[67]; (b) Cooling module based on refrigerant immersion[73].

To take full advantage of the high heat transfer coefficient of refrigerant boiling, some of the studies immersed the battery into the refrigerant and directly in contact with the refrigerant for heat exchange. Al-Zareer et al.[74] immersed the battery pack non-completely in R134a refrigerant, when the refrigerant absorbs heat to become vapor leaving the battery pack by the channel and condensing back to liquid form through the air conditioning system into the storage tank to be recycled, as shown in Fig.6(b). The charge/discharge cycle at 5C rate for 600 seconds and the Artemis highway driving cycle for 10 minutes are calculated to find that R134a can provide faster cooling for the battery, especially when the battery surface is immersed in a larger area. Based on the requirement for a compact design of the battery pack, a further small space pack arrangement was considered for the same cycle. Although the compact design slightly increases the maximum and average temperatures of the pack, it is able to keep the maximum battery temperature within a variation of 4°C for 80% of the cycles, while the maximum temperature is below 35°C[73].

Researchers have investigated refrigerant-based cooling BTMS from the battery pack cooling module structure to the design of the entire system, where indirect cooling is the major thermal management strategy currently used for the battery pack. The design of the system has enabled independent regulation of cabin and battery pack temperatures in multiple modes, and the importance of refrigerant flow regulation on system performance can be determined. However, relevant new designs have not been found in the bench test and the range of refrigerants used in the study is too narrow, with mostly R134a, a refrigerant with high global warming potential (GWP).

3.2 Fuel

HEVs use battery power and fuel as energy sources, taking advantage of the benefits of small fuel engines and battery packs to improve vehicle performance while reducing environmental impact. Fuels currently used include gasoline, hydrogen, ammonia, and propane, which need to be converted from a liquid to a gas state before entering the engine to improve the engine efficiency. Given that some fuels can meet the thermal property requirements of the battery two-phase coolant, BTMS with fuel as the coolant has also been introduced in combination with the system design of

HEVs[75]. Fig. 7 shows the application of a fuel coolant BTMS in an HEV. The pressurized liquid fuel entering the battery pack from the fuel tank is transformed into gaseous fuel by absorbing the heat generated by the battery in the form of indirect or direct cooling. The pressure regulator collects the gaseous fuel and sends it to the IC engine by creating a pressure difference through the injector. The IC engine then drives a generator to generate electricity for battery storage or an electric motor to drive the vehicle. The designed system fulfills the battery temperature control requirements and becomes a part of the HEV power system, contributing to the simplification of the HEV system and reducing the cost of the equipment.

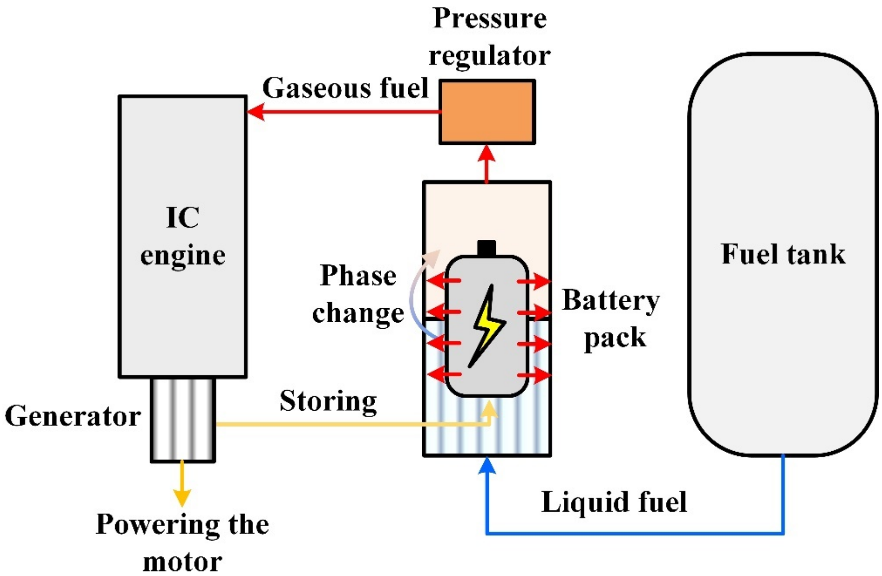

Fig. 7 Schematic diagram of fuel coolant BTMS in HEV.

Propane has a low liquid viscosity and strong thermodynamic, reflecting good flow boiling performance[76]. Existing studies have extensively explored BTMS with immersion cooling using propane as the coolant. Al-Zareer et al.[75] developed a numerical thermoelectric chemical model to investigate the effect of the propane level and saturation pressure in the battery pack on the temperature profile of the 18650 cylindrical battery. The results of the study also confirm the effectiveness of the method. The T_{max} and $\triangle T$ can be reduced by increasing the percentage of the battery length covered by propane. Furthermore, when the pressure of saturated liquid propane is increased from 8.5 bar to 10 bar, the battery temperature difference can be effectively reduced but the maximum battery temperature is increased, especially at a low propane level. Similarly, the battery spacing is also an influencing factor for the thermal performance of the battery, and four battery spacing arrangements were designed in the related study with the battery radius as the base[77]. The findings revealed that a larger battery spacing increases the $\triangle T$ between batteries while reducing the T_{max}. When the charge/discharge rate of the battery increases, the temperature performance fluctuation of the battery pack will also become larger. The same thermal management system is applied to prismatic lithium-ion batteries and a similar pattern of cooling to that of 18650 batteries was obtained. It also states that it can already provide better performance than liquid cooling systems when the battery surface coverage reaches 30%[78]. To reduce the temperature difference across each battery compared to the direct contact, the batteries were embedded in aluminum blocks with fuel pipes and the temperature difference of the battery in this system became 3.5℃, but the variation pattern is similar[79].

As a carbon-free and environmentally friendly fuel, ammonia is considered to be used in future HEVs[80]. It has been used as a BTMS coolant for 18650 battery immersion cooling. The pressurized saturated liquid ammonia covering 5% of the battery height at 9.0 bar is sufficient to keep the battery temperature below 40℃ for a high power charge/discharge cycle lasting 600 seconds at a rate of 7.5C. By increasing the height of ammonia from 5% to 30% of the battery height, the T_{max} can be reduced by 6°C[81].

It can be seen that the current analysis concentrates on the effect of battery thermal management with propane and ammonia fuel immersion cooling, and the battery temperature is effectively controlled under a variety of conditions. However, it is worth mentioning that the study of this system is only at the stage of numerical simulations, and the model calculations involved do not address the bubble behavior of the boiling process and the heat transfer effects and the actual performance of this type of BTMS has not been experimentally verified. In addition, the discussion focuses on the thermal aspects of the battery at the risk of neglecting the safety hazards of fuel applications. Considering the frequency of fuel hazards and the scale of damage, the relative risk of propane is high because of its flammability and violent combustion properties, while the main hazard of ammonia is toxicity[82]. Therefore, how to reduce the potential hazards of fuels while ensuring the thermal management performance of BTMS becomes a critical but still undiscussed issue.

3.3 Dielectric coolant

Dielectric fluids are designed to come into direct contact with cooling objects of electronics, with good insulation, thus ensuring protection when in contact with cooling objects such as electronic components. It is currently used in data center cooling, power storage facility cooling and other applications, but the coolant is expensive and has a very low thermal conductivity. Fig. 8 shows a schematic of the dielectric coolant BTMS, where the dielectric coolant is in a closed independent cycle. The supercooled coolant enters the battery pack for vaporization and heat exchange, followed by condensation of the gaseous coolant in the condenser and return to the storage tank to complete the cycle.

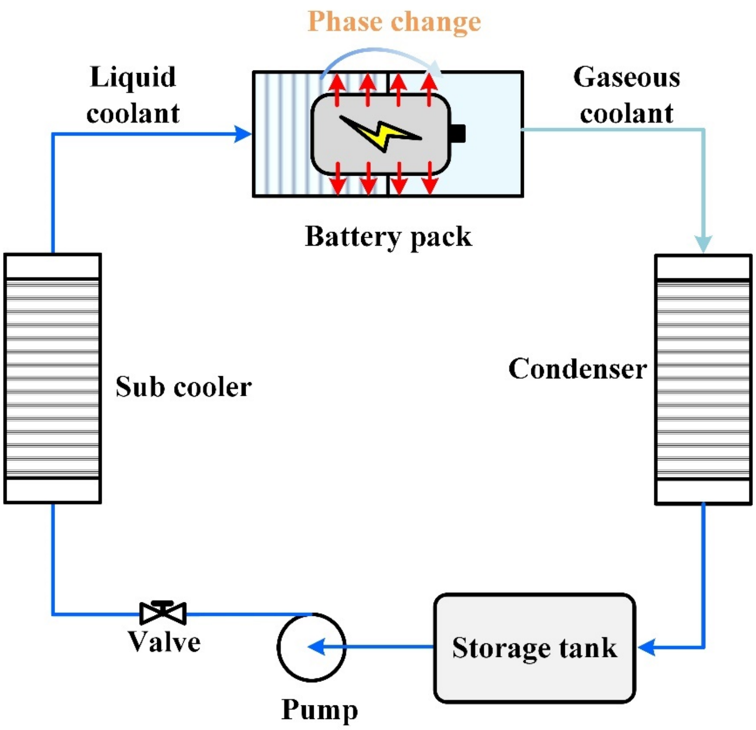

Fig. 8 Schematic diagram of dielectric coolant BTMS.

Hydrofluoroether coolant is a series of Novec products from 3M, USA. van Gils et al.[83] immersed the battery in Novec7000 coolant and conducted experimental tests on the performance of the battery. The experiments involved the boiling and non-boiling states of the starved mass. By comparison, it can be observed that the temperature difference between the positive and negative electrodes of the battery in the non-boiling state is around 0.7°C, and this temperature difference is eliminated when boiling occurs. Given that the heat balance of the coolant is closely related to the pressure, the intensity of boiling can be enhanced by reducing the pressure, thus enabling the process of active pressure regulation of heat management. Wu et al.[84] applied the same coolant to the boiling-cooling thermal management system of a large-size pouch battery and analyzed the cooling effect of coolant static and flow dynamics. The temperature and temperature difference of the battery are better improved under the condition of coolant stationary, while when the coolant turns to flow mode, the battery appears more obvious temperature difference, and this defect can be improved by intermittent flow control. An et al.[85] on the other hand, adopts a cold plate indirect cooling scheme for thermal management design, and conducts cooling experiments on the battery module at different discharge rates and flow Re numbers. Due to the better cooling effect of refrigerant, the voltage distribution of the battery module becomes more uniform, but there are fluctuations in the battery voltage at a high charge/discharge rate. The voltage value will decrease with increasing Re. Generally, for this type of system, there exists an appropriate range of Re numbers, which makes the system play a high cooling effect. Wang et al.[86] performed heat and mass transfer simulations based on the RKE two-phase flow turbulence model for the HFE7000-cooled battery pack. By analyzing the effects of battery charge/discharge multiplier and coolant inlet velocity, it can be seen that the nucleated boiling heat transfer of HFE-7000 two-phase turbulent flow is more effective in improving the temperature uniformity of the battery module, and the average heat flux at the wall of the battery is as high as 2440.06W/m^2, which is five times higher than that under single-phase convective conditions.

Table 1 compiles the performance of the two-phase coolant BTMS with different coolants and indicates that the two-phase coolant BTMS can better control the battery temperature at high operating rates than the conventional cooling system[87]. The still noticeable feature is that the temperature difference control of the batteries is variable in various systems. Compared to single-phase flow, the flow distribution and variation of multiphase flow can cause local heat transfer differences, thus deepening the battery temperature difference, so it is still necessary to analyze the two-phase mass flow characteristics in depth to find methods and strategies to improve the temperature uniformity.

Table 1 Summary and comparison of BTMS cooling performance with two-phase coolant.

Ref.	Li-ion Battery	Cooling method	Coolant	Battery load	Coverage percentage	T_{max}[℃]	△T[℃]	Key findings
[63]	2.2Ah, Cylindrical [64 cells]	Cooling tube	R134a	1.5C	/	<35	4	Refrigerant circuit optimization improves cell temperature uniformity.
[79]	18650, Cylindrical [2 cells]	Cooling block	Propane	6C	/	31.6	4.1	Cold block-cooled batteries have less temperature difference than submerged ones.
[64]	25Ah, Pouch [2 cells]	Natural convection	Air	3C	/	52.3	10.7	Two-phase coolant cooling demonstrates strong temperature suppression but requires comprehensive adjustment of operating parameters according to actual conditions.
		Cooling plate	Water	3C	/	37.6	4.4	
		Cooling plate	R134a	3C	/	31.8	5.6	
[85]	20Ah, Prismatic [14 cells]	Cooling plate	NOVEC 7000	5C	/	47.7	<4	The cooling effect can be greatly improved by the existence of a suitable Re range so that the heat transfer mode remains dominated by boiling heat transfer.
[86]	3.2Ah,	Immersion	HFE 7000	5C	/	37.1	3.6	The single-phase cooling facilitates the

	Cylindrical [60 cells]							reduction of the battery temperature, while the two-phase flow state contributes to the reduction of the battery temperature difference.
[87]	Prismatic [1 cell]	Natural convection	Air	6C	/	46.7	2.4	High enthalpy of evaporation is more conducive to lowering the maximum battery temperature
		Cooling plate	Water	5C	/	35.2	/	
		Immersion	R134a	6C	80%	34.6	9.5	
		Immersion	Propane	6C	80%	30.3	9.7	
		Immersion	Ammonia	6C	100%	25.4	3.0	
		Cooling plate	Ammonia	6C	/	27.3	4.2	
[84]	20Ah, Pouch [1 cell]	Immersion	NOVEC 7000	4C	/	<36	3.3	Intermittent flow mode can effectively control battery temperature rise and temperature difference with low pumping work.

4. BTMS based on heat pipe

Heat pipes are considered to be a passive element that uses the latent heat of vapor-liquid phase change because the circulation process of the working medium does not require external components to drive or energy input. The basic heat transfer principle of the heat pipe in the battery module is shown in Fig. 9.

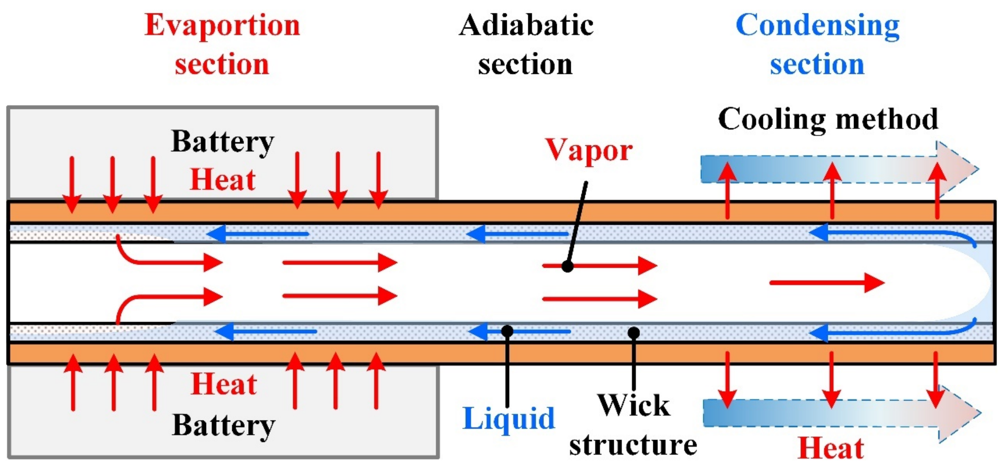

Fig. 9 Heat transfer principle of the heat pipe in battery module.

The working medium evaporates at ambient temperature and absorbs heat from the battery, and the vapor flows rapidly to the condensing section to condense and exotherm under the influence of the cooling method. The porous wick inside the heat pipe is designed to pump the cooling liquid back to the evaporating side by the capillary property, to realize the phase change and circulating flow of the working medium inside the heat pipe. The circulation of the working medium determines the long-term operating of the heat pipe, where the capillary pressure difference provided by the wick is the key guarantee of the whole circulation. The internal flow of the heat pipe in normal operation should satisfy the following relations[88]:

$$\Delta P_{mc} \geq \Delta P_v + \Delta P_l \pm \Delta P_g \tag{4}$$

where ΔP_{mc} is the maximum capillary pressure difference that the porous wick can provide. ΔP_v, ΔP_l represent the vapor flow pressure drop, and the liquid fluid flow pressure drop, which are related to the heat transferred by the heat pipe, the working medium properties, and the internal channel structure of the heat pipe, especially the thickness. ΔP_g is the effect of gravity on the flow, where ΔP_g is negative when gravity can help the liquid fluid reflux. Therefore, the heat transfer performance of the heat pipe can be changed by the external heat input, ambient temperature as well as other factors, and there are also limits of heat transfer. The cooling method on the condensing section of the heat pipe is usually air cooling or liquid cooling, and the system schematic is shown in Fig. 10. After years of development, it is possible to design and manufacture heat pipes of various configurations. The following types of heat pipes have been applied to the thermal management of EVs.

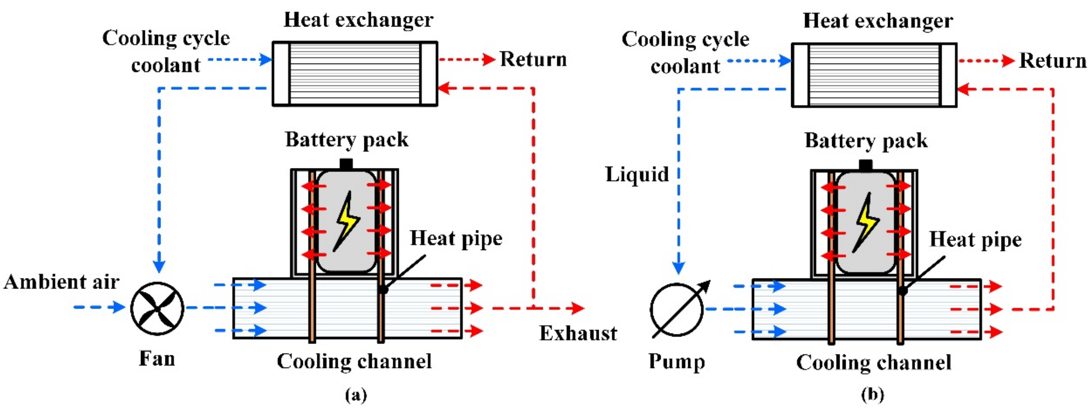

Fig. 10 System design diagram of heat pipe based BTMS: (a) Heat pipe based air cooling BTMS; (b) Heat pipe based liquid cooling BTMS.

4.1 Typical heat pipe

As one of the most typical heat pipes, cylindrical heat pipes are usually processed on the tube wall with capillary characteristics as porous wick, such as groove, sintered copper powder, wire mesh, and then sealed, filled with liquid and vacuumed[89]. Because of the tubular shape, the contact area between the heat pipe and the battery directly can be disadvantageous to heat exchange. Therefore, the technical solution usually adopted is to increase the heat-conducting components to improve the contact area between the heat pipe and the battery. Greco et al.[90] developed a one-dimensional transient simplified model for a battery module consisting of a grooved-wick heat pipe and a prismatic battery using a thermal loop approach based on the thermal management system of Fig. 11(a). The reliability of the model is verified by comparison with the 3D numerical simulation results while the advantages of heat pipe cooling and forced convection are equally established. In addition to increasing the contact area, enhancing the cooling efficiency of the condensing section of the heat pipe is a commonly attempted approach. Tran et al.[91] inserts the evaporative section of multiple heat pipes into aluminum blocks and installs fins in the condensing section to enhance heat exchange with flowing air. By evaluating the temperature performance of the module under different inclinations and convection conditions, it is clear that in combination with forced air convection, the heat pipe provides better heat dissipation performance, but the increase in air speed does not effectively improve the heat dissipation performance. E et al.[92] analyzed the influence of structural parameters of fins to quantify the influence of fin spacing and thickness on heat transfer coefficient, so as to determine the optimal design parameters and air inlet parameters suitable for battery packs. Gan et al.[93] uses a wavy aluminum sleeve to connect the battery to the heat pipe to increase the contact area between the battery and the heat pipe, and bends the cylindrical heat pipe 90° to enhance the heat transfer with the fit of the liquid cooling plate. The structure of the system is displayed in Fig. 11(b). Findings show that increasing the length of the heat pipe condenser section and the height of the aluminum jacket improve the temperature and temperature difference of the battery pack, while the coolant flow rate has a more significant effect on the maximum temperature.

Although the above approach can compensate for the disadvantages of cylindrical heat pipes, it is not conducive to the design concept of compact systems. In this regard, a proposal is made to improve the conventional heat pipe shape. After the conventional process of the heat pipe is completed, the heat pipe can be flattened to a suitable thickness by a flattening process at a certain temperature and flattening force, despite the potential loss of the heat transfer performance of the heat pipe[88]. Feng et al.[94] applied the flattened heat pipe to 18650 cylindrical batteries and tested the temperature and strain during steady-state and dynamic discharge conditions, while also specifying the importance of convection conditions on thermal management performance, with a 15°C reduction in battery temperature and 50% reduction in strain through forced convection. Behi et al.[95, 96] conducted numerical simulations and experiments on lithium titanate (LTO) batteries and demonstrated that heat pipes are more effective in reducing battery temperature than single conventional cooling, whether coupled with air cooling or liquid cooling. Alihosseini et al.[97] adopted a 3mm thickness heat pipe combined with liquid cooling for the battery module shown in Fig. 11(c) and selected a battery in the module as the simulation domain. The study determined the influence law of ambient temperature, where the average temperature of the battery surface increased by 2°C, 5°C and 8°C at ambient temperatures of 33°C, 28°C and 18°C, respectively. Han et al.[98] proposed a BTMS with a heat pipe assisted hybrid fin structure, without increasing the space of the original system. Compared with the common fin system, the total thermal resistance of this system is reduced by 13.7% under fast charging conditions. When the thickness of a heat pipe reaches 2 mm or less, it is defined as an ultra-thin heat pipe. Liu et al.[99] developed a "segmented" thermal resistance model of an ultra-thin heat pipe and integrated it into a thermal model of a forced convection air-cooled battery pack. Considering that the thermal impact of the positive electrode is larger than that of the negative electrode, the condensing end of the heat pipe near the positive electrode can better suppress the maximum temperature by taking advantage of its efficient heat transfer.

In order to ensure the fit and heat transfer between the heat pipe and the battery, a partially flattened heat pipe is made by flattening the part of the heat pipe that attaches to the battery, while maintaining the shape of a cylindrical tube in the condensing section. Ye et al. [100] focused on air-cooled partially flattened heat pipe BTMS systems, but the results of the study showed that the pack temperature could not be achieved during fast charging, and increasing the number of heat pipes did not necessarily improve the temperature uniformity. Liang et al.[101] combined the partially flattened heat pipe with liquid cooling, as demonstrated in Fig. 11(d). This system can effectively enhance thermal management by reducing the coolant temperature. Moreover, the battery temperature and temperature difference can be controlled within the desired range by intermittent start-stop of the coolant, thus reducing the running time of the system and reducing power consumption. Meanwhile, the electrochemical-thermal coupling three-dimensional model of the series battery module with heat pipe cooling was established. From the perspective of battery electrochemical performance, it can be found that the decrease in coolant temperature will affect the Li^+ in the positive solid phase of the battery, resulting in the loss of the available capacity of the battery[102].

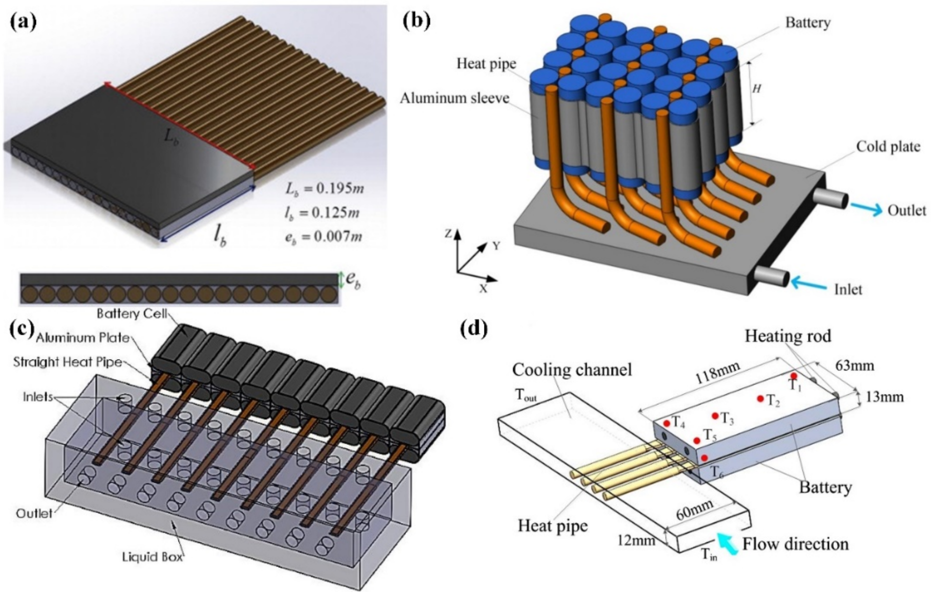

Fig.11 Typical heat pipe cooling:(a) Cylindrical heat pipe with air cooling[90]; (b) L-shaped cylindrical heat pipe coupled with cold plate[93]; (c) Flattened heat pipes with immersion cooling [97]; (d) Partially flattened heat pipe with immersion cooling[101].

Wang et al.[103]focused the analysis on the structural design of the thermal management system with partially flattened heat pipes, and obtained the sensitivity of parameters such as battery spacing, conduction element thickness, the circumference angle between the battery and conduction element to optimize and determine the structure with the best heat transfer performance. And a heat pipe based thermal equivalent circuit model of the BTMS has been proposed successively to realize the rapid prediction of the thermal management system performance[104]. Mbulu et al.[105] investigated a battery thermal management system based on L-type and I-type flattened heat pipes, using water as a coolant to cool the battery when operating at high input power. The designed BTMS showed good thermal management performance over a 2-hour test period, with about 92.18% of the heat transferred from the high-heating battery by the BTMS.

Table 2 summarizes the performance of various typical heat pipe based BTMS. The copper-water heat pipe with mature technology, low cost, and non-polluting workpiece was mainly used in this study, and good heat transfer results were achieved in various system configurations Although the contact area of the heat pipe was improved by the flattening treatment, the BTMS still requires a large number of heat pipes and accessories to ensure the temperature uniformity of the battery due to the constraints of tube diameter and wall thickness, so the complexity and economy of the BTMS still need to be optimized and considered in the future.

Table 2 Summary of BTMS performance based on typical heat pipes

Ref.	Li-ion Battery	Battery load	Heat pipe	Working medium	Shell material	Thickness	Cooling method	T_{max}[°C]	△T [°C]	Key findings
[90]	ePLB C020, Prismatic [1 cell]	5C (40.95W)	Typical	Ammoniac	/	5mm (Diameter)	Air cooling	27.6	<2	Prove the effectiveness of heat pipe cooling
[95]	23Ah, Prismatic [1 cell]	8C	/	/	/	/	Natural air cooling	55~57	≈5	Forced air cooling effectively reduces the maximum battery temperature
			Flattened	Deionized water	Copper	3.5mm	Forced air cooling	38.9	≈5	
[96]	23Ah, Prismatic [15 cells]	8C	Flattened	Deionized water	Copper	3.5mm	Liquid plate	38.2	/	
[98]	16 Ah, Prismatic [4 cells]	3C	Flattened	Deionized water	Copper	3 mm	Liquid plate with fins	≈43.2	≈3.7	The design of the condensing side of the heat pipe on the cold plate is important for the maximum temperature
[99]	Pouch [5 cells]	3C	Flattened	Deionized water	Copper	1 mm	Forced air cooling	43.9	4.3	Optimizing the placement of heat pipes can effectively suppress the

									maximum temperature
[93]	2.95Ah, Cylindrical [24 cells]	2C	Bendable	Deionized water	Copper	6.7 mm (Diameter)	Cooling plate	31	4.6	Increasing the length of the condensing section of the heat pipe can improve thermal management
[102]	6Ah, Prismatic [4 cells]	5C	Partially flattened	Deionized water	Copper	2 mm(Flattened) 6 mm(Diameter)	Liquid immersion	<34.8	3.1	Lower coolant temperature leads to loss of battery capacity.
[103]	1.96Ah, Cylindrical [3 cells]	3C	Partially flattened	Deionized water	Copper	2 mm(Flattened) 6 mm(Diameter)	Liquid immersion	27.6	1.08	Component optimization to improve BTMS thermal performance.

4.2 Micro heat pipe array

Micro heat pipe array refers to a type of heat pipe that is manufactured by extrusion with multiple independent microchannels inside, the structure and operating principle are shown in Fig. 12. Since each microchannel is not interoperable and can operate independently based on the heat pipe operating principle, the failure of a single microchannel has little impact on the performance and offers a high level of reliability[106, 107]. Compared with flattened heat pipes, the length and width of the micro heat pipe array can be designed flexibly according to the demand, which can have a larger heat exchange area with the battery.

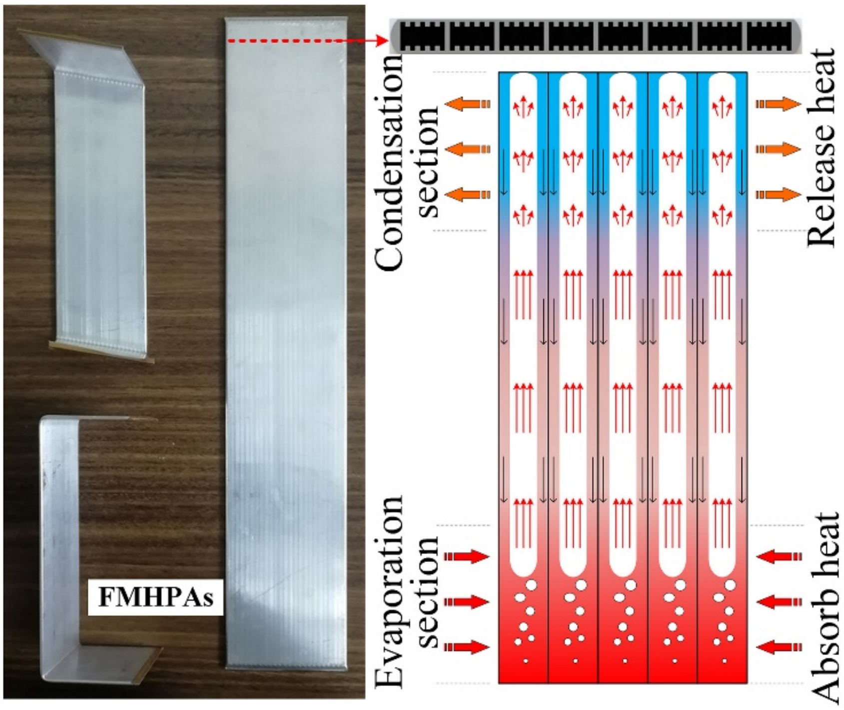

Fig.12 The basic structure and working principle of micro heat pipe array[107].

Ye et al.[108]verified the effectiveness of the micro-heat pipe array in controlling the temperature difference of the $LiFePO_4$ battery pack at a discharge rate of 1C, and the results also confirmed that both the installation of fins and the enhancement of forced convection intensity can significantly reduce the surface temperature difference of the battery. Wang et al.[109] modeled a three-dimensional numerical model of battery heating based on micro-heat pipe arrays and calculated that the designed micro-heat pipe arrays could raise the battery pack temperature from -30°C to 0°C with a maximum temperature difference of less than 3.03°C within 20 minutes. Dan et al.[110] developed an equivalent thermal resistance model based on the heat transfer loop of the micro heat pipe array and combined it with the lumped thermoelectric model to predict the transient temperature characteristics of the battery pack based on the cooling of the micro heat pipe array as shown in Fig. 13(a).

Except for the conventional flat profile, micro heat pipe arrays can be processed into other shapes to meet the design requirements of the battery pack. And some methods to enhance the heat transfer of micro heat pipes have been attempted. Zhao et al.[111] added liquid droplets to the cooling air to create evaporation-enhanced heat transfer on the heat pipe condensing section. The wet cooling proved to be effective, the temperature difference between the battery pack and the center battery was less than 1.5°C and 0.5°C, respectively, under all operating conditions. Zhang et al.[112] made the micro heat pipe array into an L-shape, similarly using wet air across the condensing section of the heat pipe, and the wet air is not in contact with the battery, as illustrated in Fig.13(b). In this study, the maximum temperature of the battery at 3C discharge rate was controlled at 36.27°C, while the maximum temperature difference of the battery pack reached 15.68°C. In addition, the humidity of the wet air increases in favor of the even temperature, but the battery temperature also increases. Ren et al.[113]designed the micro heat pipe array in a U-shape to wrap the battery pack tightly and improve heat dissipation performance through two condensing sections, with heat carried away by airflow. The system is provided with both cooling and heating modes as shown in Fig. 13(c). Even under constant discharge conditions of 2C and 3C the battery temperature is lower than the warning temperature, and the active air cooling mode can control the battery temperature difference to less than 5°C. The effectiveness of the system in low-temperature environments was analyzed experimentally. In the preheating stage, higher electrical heating power results in lower temperature uniformity of the battery, and the micro-heat pipe array increases the holding time from 5.45 h to 8 h[114].

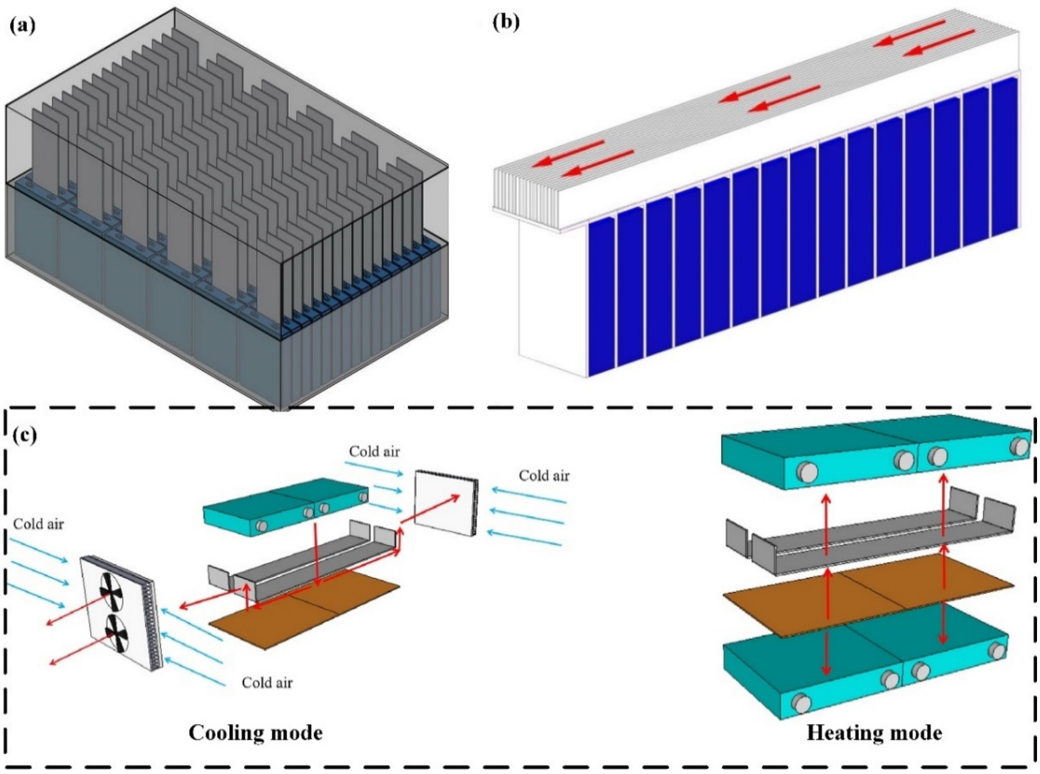

Fig.13 BTMS applying micro heat pipe array: (a) Micro heat pipe array with air cooling[110]; (b) L-shaped micro heat pipe array with air cooling[112]; (c). Cooling and heating mode of U-shaped micro heat pipe array[114].

Zeng et al.[115] tried to combine liquid cooling technology and micro heat pipe array into a cooling module, which can reduce the maximum temperature and temperature difference of the battery pack to 41.03℃ and 2.16℃ respectively under the experimental condition of battery discharge rate of 3C. At the same time, the optimization method based on multi-objective optimization improves the energy density of the system by 13.75% and maintains the original cooling performance.

Micro-heat pipe arrays are mainly combined with air cooling to form BTMS, and the concept of wet air cooling and the heating mode of BTMS have been explored successively. As shown in the results of Table 3, the micro-heat pipe array is effective in reducing the high temperature of the battery, and the shaped structure can effectively improve the heat pipe on the volume expansion and mass increase of the BTMS. Future attempts can be made to combine with liquid cooling and explore the system performance for conditions such as extremely fast charging.

Table 3 Summary of BTMS performance based on micro heat pipe arrays

Ref.	Li-ion Battery	Battery load	Heat pipe shape	Thickness	Cooling method	T_{max}[℃]	△T [℃]	Key findings
[108]	18Ah, Prismatic [16 cells]	1C(20.8W)	/	/	Nature convection	<45.4	6.1	Micro heat pipe array takes 3/4 of the heat produced by the battery
			Flat	3mm	Forced air cooling with fins	<34	<2	
[111]	3Ah, Prismatic [4 cells]	3C	Flat	2 mm	Forced air cooling	31.8	6.7	Wet air cooling can effectively improve battery temperature
			Flat	2 mm	Wet air cooling	21.5	2.5	
[112]	22Ah, Prismatic [15 cells]	3C	L-shape	3 mm	Wet air cooling with fins	36.27	15.68	Wet air cooling available with imported humidity to adjust battery temperature
[113]	120Ah, Prismatic	3C	U-shape	2.5 mm	Forced air cooling	51.7	<4.8	U-shaped micro heat pipe array increases battery system volume by only 2.5%

4.3 Vapor chamber

The vapor chamber is a kind of flat heat pipe derived from heat pipe. In the manufacturing process, the wick structure is sintered on the etched or stamped upper and lower shell plates, which are combined to form a closed space through a welding process, followed by a similar manufacturing process of heat pipe such as liquid injection and vacuuming[116]. In this process, the design of the vapor chamber is more flexible in terms of shape, internal wick and support structure, which can be made of either shell material or wick structure. Benefiting from the larger vapor flow space and the flexible design of the vapor-liquid channel, the vapor can carry heat to diffuse quickly, thus facilitating the elimination of hot spots in the heat source and providing better uniform temperature performance, as shown in Fig. 14.

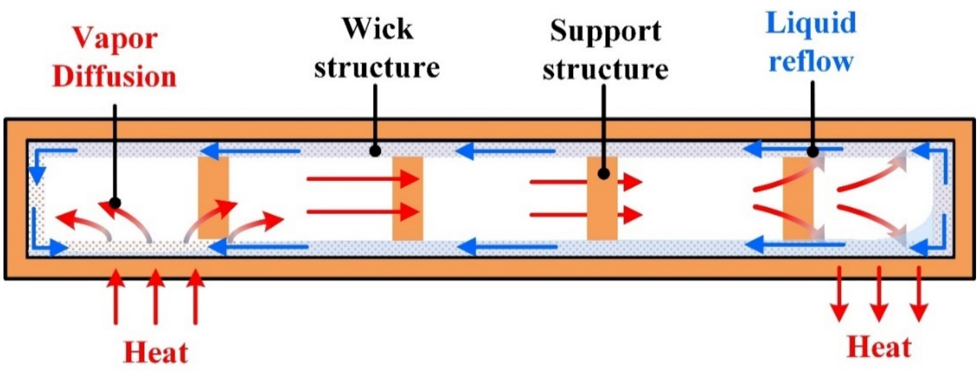

Fig. 14 Schematic diagram of the transverse heat transfer in the vapor chamber.

Kim et al.[117] studied an aluminum vapor chamber with dimensions of 138x 90 mm^2 and a thickness of 4 mm and analyzed the effect of filling rate in the vapor chambers. The thermal resistance of the aluminum vapor chamber at the optimum filling rate was reduced by 90% compared to that of the pure aluminum plate, and its superior performance in heat transfer was directly demonstrated in the comparative tests of the actual battery. Cheng et al.[118] explored the preheating function of liquid-cooled vapor chamber BTMS at -10°C ambient temperature based on the cooling mode. By increasing the heating medium temperature, the battery heating time can be accelerated, but the temperature uniformity is also reduced. Liu et al.[119] proposed a battery thermal management system for cylindrical Li-ion battery packs based on a combination of the vapor chamber and fin structure. At an ambient temperature of 25°C, the vapor chamber can significantly reduce the average temperature rise of the battery at different discharge rates of 2C, 3C and 5C, improving the uniformity of temperature distribution within the battery pack. As for the combination of vapor chamber and liquid cooling, the effect of uniform temperature can be more powerful.

In order to improve the applicability of heat dissipation in batteries, shaped vapor chambers are designed and used in batteries. Gou et al.[120] designed a new three-dimensional vapor chamber consisting of three interconnected but non-coplanar vapor chamber. The study first determined the effect of liquid charge rate on the performance of the vapor chamber, and the study on the effect of road conditions found that the tilt angle and position of the system have no significant effect on the cooling effect of the battery. Luo et al.[121] proposed a new type of vapor chamber consisting of five heat pipes compounded with a vapor chamber. The start-up characteristics and heat transfer performance of the plate were compared under different heat flow densities and coolant flow patterns to determine the best performance range. The effectiveness of the vapor chamber in preheating and cooling the battery was also confirmed.

The application exploration of vapor chamber in BTMS mainly includes the working medium, working condition, and new 3D design, but all around the conventional scale of vapor chamber design. The vapor chamber has been able to achieve efficient heat transfer in ultra-thin size through structural design and processing to enhance the compactness of system[122-124]. Therefore, the future application of ultra-thin vapor chamber in BTMS will become the main research content, including the internal structural design of ultra-thin vapor chambers adapted to the heat production characteristics of batteries, the design of BTMS with a compact structure and the performance optimization strategy.

4.4 loop heat pipe

The loop heat pipe is an efficient phase change heat transfer device that separates the vapor and liquid and forms a vapor-liquid loop. The separation of the vapor-liquid flow paths provides for low vapor-carrying resistance, fast start-up, and long multi-directional heat transfer in the loop heat pipe. Fig. 15(a) illustrates the basic structure of the loop heat pipe.

Putra et al.[125] made the loop heat pipe into a flat plate type, using a stainless steel screen as a capillary wick, which was filled with distilled water, alcohol and acetone at 60% of the filling rate, respectively. The flat-plate loop heat pipe could be started at heat flow loads as low as 0.48 W/cm^2, and temperature overshoot was observed during start-up. The flat-plate loop heat pipe performed best at a heat flow load of 1.61 W/cm^2 with acetone as the working fluid with a thermal resistance of

0.22 W/℃. Hong et al.[126] applied air cooling to a 1.5mm thick flat loop heat pipe, as shown in Fig. 15(b), and conducted a series of experiments with different condensation conditions to find out the best condensation conditions for the flat loop heat pipe. Bernagozzi et al.[127] places several graphite sheets between the batteries, which act as thermal conductors to transfer heat to the flat loop heat pipe at the bottom of the battery module and eventually to the HVAC chiller with the system shown in Fig. 15(c). The design meets the battery thermal requirements at both pack and battery levels. The maximum battery temperature at fast charge is 31.5 ℃, which achieves a maximum temperature reduction of 2 ℃ compared to the liquid-cooled plate results.

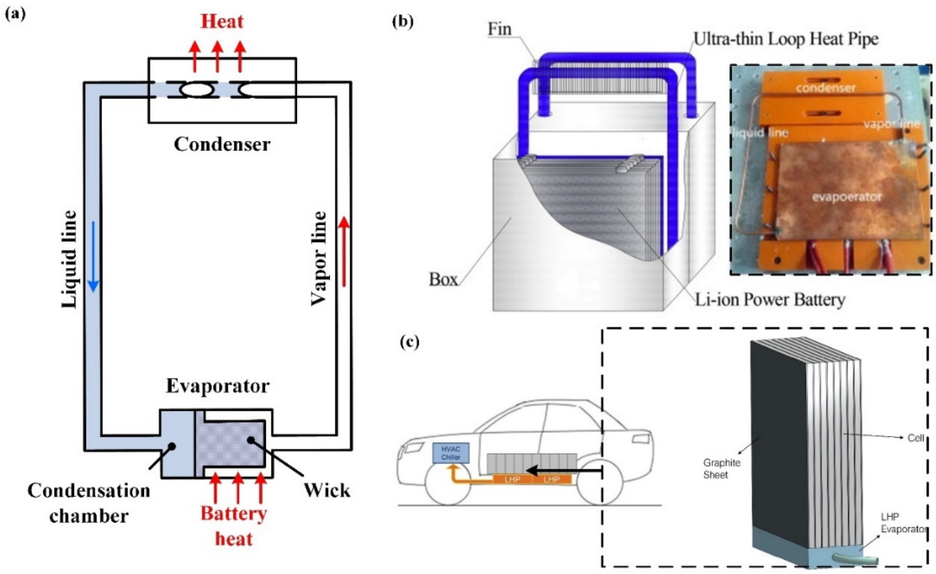

Fig.15 BTMS applying loop heat pipe: (a) Schematic diagram of loop heat pipe principle; (b) Loop heat pipe placed between batteries[126];(c) Loop heat pipe at the bottom of the battery[127].

Hashimoto et al.[128] explored the preheating effect of the loop heat pipe on the battery and established a new transient analysis model. The experimental verification can find that the battery rises from -20℃ to 0℃ in about 14,600s with a ramping rate of 0.06~0.09℃/min. Bernagozz [129] evaluated the possibility of an EV system consisting of a heat pump and a loop heat pipe, and developed a one-dimensional lumped parameter model to predict the transient behavior of the loop heat pipe.

Most of the studies have been conducted with simulated batteries as the heat source and more attention has been paid to the thermal performance of the loop heat pipe, as it involves critical issues such as start-up and thermal leakage. Although these results can inform the design of BTMS, the battery performance and the impact of real-time changes in thermal load on the loop heat pipe operation remain to be evaluated.

4.5 Pulsating heat pipe

The pulsating heat pipe is a heat pipe without a wick, and the structure is designed as a serpentine tube. After being heated at the evaporation section, the fluid transforms into a vapor plug inside the tube, which pushes the liquid to the condensing side to form a phenomenon of high-speed oscillation of the two phases inside the tube.

Rao et al.[130] analyzed the effect of pulsating heat pipes on battery heat dissipation experimentally and clearly stated that pulsating heat pipes need to be placed vertically to reduce the resistance of the working medium to reflux. Wei et al.[131]filled the pulsating heat pipe with different ratios of ethanol and water mixture and analyzed the variation of pulsating heat pipe starting power and battery module temperature. By determining the appropriate solution ratio, the temperature difference of the battery with a heat generation capacity of 56W can be controlled to 1-2℃.

Chen et al.[132] used water-based Tio nanofluid as the working medium of the pulsating heat pipe and confirmed the superiority of heat transfer of the nanofluidic medium. Under different temperature conditions, the battery temperature was suppressed and the temperature uniformity was improved by 60% using air cooling as an aid, as shown in Fig. 16. Zhou et al.[133] made a nanotube-based nanofluid pulsating heat pipe, which is better in thermal resistance and starting temperature compared to ethanol pulsating heat pipe, further reducing the temperature and temperature difference of the battery. As can be seen, the heat transfer performance of the pulsating heat pipe can be improved by adjusting the working medium type, liquid filling rate, and structural parameters, which can contribute greatly to the thermal control of BTMS. However, a limitation of the pulsating heat pipe application is the long design of the condensing section and the need for vertical placement, so that the required design volume of the battery pack is oversized.

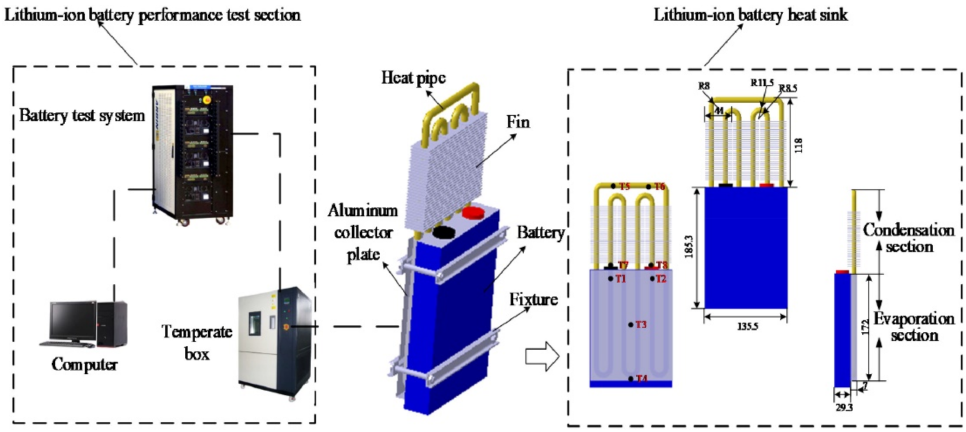

Fig.16 BTMS for pulsating heat pipe cooled batteries[132]

Table 4 summarizes several BTMS based on vapor chamber, loop heat pipe, and pulsating heat pipe, which are still in the preliminary stages of discussion in recent years. These heat pipes all demonstrate usable value in BTMS but still need to be further developed to fit the BTMS trend. The development of coupling models between the battery and these heat pipes is needed to better understand the coupled heat transfer mechanisms and to clarify the heat transfer patterns of the heat pipes and the battery. This can lead to the improvement of heat pipes and the design of BTMS into an applicable technology.

Table 4 Summary and comparison of BTMS performance based on heat pipes

Ref.	Li-ion Battery	Battery load	Heat pipe type	Thickness	Cooling method	T_{max}[℃]	△T [℃]	Key findings
[118]	Prismatic [4 cells]	3C(51.84W)	Vapor chamber	3 mm	Liquid plate	38	6.5	37.5% reduction in maximum temperature compared to cold plate cooling
[126]	50Ah, Prismatic	2.5C	Loop heat pipe	1.5 mm	Air cooling	<55	/	The loop heat pipe can be activated at lower heat flux and lower temperatures
[127]	65Ah, Prismatic	Fast charge from 20% to 80% SOC in 10 min	Loop heat pipe	10 mm	Liquid cooling	31.5	2	Enables remote heat transfer with air conditioning heat exchangers
[132]	68Ah, Prismatic	1.5C	Pulsating heat pipe	7 mm	Air cooling with fins	44.84	1.52	BTMS performance enhanced with nanofluid

5. BTMS based on PCMs

PCMs represent a type of material that uses latent heat to store and release heat through state transitions of the material. Various types of phase change materials have been developed, which can be broadly classified as organic PCMs, inorganic PCMs and eutectic PCMs. Depending on the operating temperature of the phase change and the properties of the material, PCMs have been used in critical areas such as thermal storage systems[134], building energy saving[135], and photovoltaic devices[136]. Similarly, in the field of EVs, it is proposed to make use of PCMs to absorb the heat generated by the battery during operation, thereby achieving a constant battery temperature. In order to meet the requirements of EV battery systems, PCMs should also fulfill several conditions including high latent heat and thermal conductivity, safety, stability and slight volume change during phase change, good economics and processability[24]. Fig. 17 shows a schematic of a PCM-based BTMS, in which the PCM wraps around the battery pack and, similar to a heat pipe BTMS, can be combined with air cooling or liquid cooling for heat dissipation.

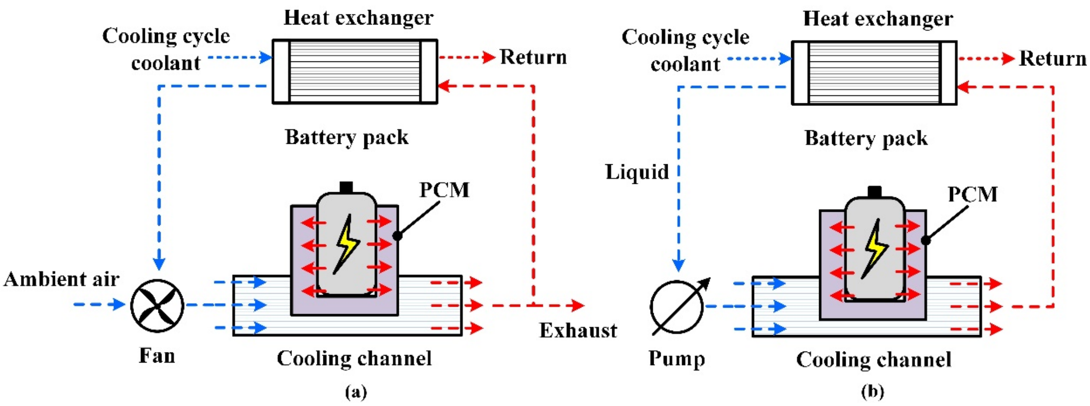

Fig. 17 System design diagram of PCM based BTMS: (a) PCM based air cooling BTMS; (b) PCM based liquid cooling BTMS.

5.1 Organic PCMs

Organic PCMs are usually divided into two types: paraffin(PA) and non-paraffin, of which paraffin is characterized by no corrosion, no phase separation, low cost and phase change temperature suitable for the operating temperature of the battery but flammable. Since it is an n-alkane, the melting point and latent heat can be increased by increasing the length of CH_3 chains, which can adjust the latent heat of PAs[137]. Non-paraffin phase change materials are classified as fatty acids, sugar alcohols and glycols, which are characterized by high latent heat and compatibility with packaging materials, but the materials are not stable at high temperatures and cost more expensive than PA[138]. Nevertheless, organic PCMs are characterized by low thermal conductivity in general as well as melt-prone leakage, which are also addressed in the relevant research focus.

Javani et al.[139] designed thin layers of pure PA PCMs of different thicknesses to surround lithium-ion power batteries and performed numerical calculations. The added PCMs play a leading factor in the effect of battery temperature. The hot spot on the battery shifts from the bottom to the middle as the thickness of the PCMs increases, while the average temperature decreases slowly. Based on the results, an effective index of PCM cooling effect is proposed as followed:

$$\text{cooling effectiveness}=\frac{T-T_{ave}}{T_{max}-T_{ave}} \tag{5}$$

where T_{ave} is the volume-average temperature of models, T_{max} is the maximum temperature of models. Qin et al.[140] designs a cylindrical battery thermal management system based on aluminum jacket loaded with high melting point graphite (RT56). The thermal management system combines the active mode with the fan and the passive mode with natural convection heat dissipation. It is shown that when the battery discharge rate is 3C, the maximum temperature of the battery in the passive mode exceeds 40°C, while the active mode with forced air convection cooling can meet the temperature limit of the battery. Yan et al.[141] compared the effect of different phase change temperatures (36°C, 45°C, and 58°C, respectively) of PA in the BTMS. The PCM thermal management system was successful in eliminating the temperature peaks of the battery pack and was more effective than the air cooling system. The PCM with a phase change temperature of 45°C better controlled the battery temperature in the required range when the battery discharge rate reach 3C, which is also due to the combined effect of the latent heat difference between the materials and the battery temperature. Since thermal management systems all have a certain response time to the cooling of the heat source, namely the time required to reach a specific temperature, also known as the delay effect[142], Talele et al.[143] developed a predictive multi-optimization model to predict the delayed behavior effect trajectory by using ANN methods and Least square linear regression models. Model calculations show a strong correlation between the time delay effect and the liquid fractionation rate, with the delay time increasing with the liquid fractionation rate. For RT-18, the liquid fractionation rate is consistently lower than that of PA at different discharge rate. Therefore, PA takes longer to reach the set threshold temperature.

Non-paraffin-based organic PCMs are also involved in thermal management related studies. Verma et al.[144] numerically evaluated the effect of capric acid as a

PCM for batteries. At the same battery heat generation, the capric acid with 3mm thickness can control the battery temperature in the ambient environment to 39°C; while when the ambient temperature rises to 50°C, the material has poor heat dissipation performance. Additionally, a comparison of capric acid with PA shows that capric acid reduced the battery temperature to a lower level than PA at a thinner thickness. Koyama et al.[145] selected trimethylolethane (TME) hydrate with a melting point of 30°C as a thermally managed PCM, and measured the latent heat and equilibrium temperature of TME at mass fractions of 0.2 to 0.8. The optimum mass fraction was determined to maximize the latent heat of TME and to avoid solid precipitation of TME.

The low thermal conductivity of PCMs has been considered as a limiting factor for their applicability, due to the prolonged heat release time and transfer time. Incorporating high thermal conductivity materials into the formulated PCM or combining high thermal conductivity components including copper foam, metal mesh, and fins are the main approaches at present[26]. Wang et al.[146] experimentally compared the cooling effect of pure PA and PA/aluminum foam PCM in the battery system. The addition of aluminum foam makes the theoretical effective thermal conductivity 218 times higher than that of pure PA, so it accelerates the melting process of PA and reduces the temperature difference of the battery. Qu et al.[147] developed a two-dimensional transient model for a passive BTMS considering the electrochemical properties of the battery as well as the PA solid-liquid phase variation. The model considers the natural convection and thermal non-equilibrium effects of molten PA within the copper foam and verifies the effect of the combination of copper foam and PA on the reduction of the battery. As shown in Fig. 18(a), copper dutch weave was added to the container along with PA in the study and significantly reduced the battery temperature by 10°C, effectively solving the resistance problem between the battery and the porous metal/PCM[148].

The application of high thermal conductive materials is also a popular approach nowadays, where expanded graphite(EG) is a common additive for PCMs and can have the effect of reducing leakage[149]. Considering the existence of thermal resistance at the interface between EG and PCM, Wu et al.[150] used the enthalpy method to model the EG and PA composites using the single-temperature energy equation with equivalent physical properties, and demonstrated the effect of EG incorporation on heat transfer. In addition, the thickness of the composite PCM and the intensity of heat transfer from the outside greatly affect the cooling effect of the battery, where the cooling effect brought by enhanced convective heat transfer is more limited. Liu et al.[151] experimentally discusses the heat dissipation effect of three composite PCMs with different phase transition temperatures on overcharged batteries. The results reveal that the application of PCM can slow down the temperature increment of the overcharged battery, which can reduce the battery temperature by 10°C in the early stage of overcharge. Similar to the normal charging process, a suitable phase change temperature can reduce the battery temperature more effectively. Nanomaterial-enhanced PCM has also been tried for BTMS. Bais et al.[152] added Al_2O_3 nanoparticles into PCM(RT-42) at the optimal thickness and found that increasing the weight fraction (wt) of the nanoparticles promoted the melting of PCM and increased the maximum temperature of the battery. Jilte [153]explored the feasibility of bilayer nanoparticle-reinforced PCM with the aim of extending the time and temperature adaptation range of heat absorption. The design can control the temperature rise of the battery at a high temperature of 40°C to 6°C. Zou et al. [154]used carbon nanotubes and graphene as additives to synergistically optimize the thermal conductivity and phase transition time of the PCM. This PCM has similar effective thermal conductivity as the copper foam-based PCM but at a 90.3% cost reduction[155]. Zhang et al.[156] considered aluminum nitride(AlN), a substance helpful in promoting heat transfer, as an additive to the composite PCM. The study determined the effect of AlN on the enhancement of material mechanics, thermal conductivity, and volumetric thermal resistivity. The maximum enhancement of tensile, flexural and impact strengths was observed at 20 wt% AlN addition.

Further, the mechanical properties of the material are also an important factor to be considered in practical applications, especially in response to thermal runaway or crash situations. Luo et al.[157] formed a new PCM by combining PA, EG and epoxy resin(ER) in a 5:2:3 mass ratio, and the ER increased the mechanical properties of the material. Even under 6 extreme charge/discharge cycles, the maximum temperature of the battery is still limited to below the safe temperature, and safety was ensured when the PA was completely melted. Wu et al.[158] tested the mechanical properties of the composite PCM doped with ER and found that the tensile strength, flexural strength and compressive strength of PA/EG/ER were increased by 4.4 times, 2.9 times and 3.0

times, respectively, compared with PA/EG. A new strategy of replacing the bulky rectangular PCM module construction with a tubular PCM cell is shown in Fig. 18(b), which resulted in an increase in the energy density of the battery module from 75.5 Wh kg^{-1} to 94.4 Wh kg^{-1}. Lv et al.[159] has combined EG and low density polyethylene (LDPE) with PA to form a ternary composite PCM, coupled with low fins to form BTMS. LDPE not only effectively prevents PA leakage and enhances the mechanical properties of the material, but also significantly improves the temperature performance of the battery pack under 3.5C discharge conditions, which is better than the combination of PA and EG.

The flexible properties of PCM are also being developed, which on the one hand facilitates the installation of the material in the application object and on the other hand benefits the reduction of the contact thermal resistance. Wu et al.[160]adapted olefin block copolymer(OBC) to PA/EG and demonstrated good physicochemical compatibility. The flexibility of the material was achieved by the unique structure of OBC, which mainly exploits the mechanism that the liquid phase causes changes in the chain mobility of the continuous phase during PA melting. The flexible PCM is fixed to the battery by an interference fit without adding thermal conductive silicone grease, as illustrated in Fig. 18(c). The temperature variation of the PCM is low within the acceptable range under DST and charge/discharge cycle conditions, while the battery temperature is well controlled[161]. Huang et al.[162] replaced the support material of the composite PCM with styrene butadiene styrene (SBS). The composite PCM also reflects good flexibility and elasticity, while the range of flexural strength is related to the ratio of PA and SBS, and EG in the range of mass fraction less than 4% can effectively improve the heat transfer performance of the material. In general, the composite PCM offers remarkable thermal performance. To further pursue the leakage resistance and vibration resistance of the material, Ethylene-Propylene-Diene Monomer is cross-linked with SBS to enhance the adsorption capacity of PA. The composite PCM maintains good thermal performance and also maintains a tight fit to the battery under frequent vibration conditions at 20 Hz, keeping the maximum temperature fluctuation of the module less than 2℃[163]. Yang et al.[164] synthesized a new flexible PCM with good room temperature flexibility using thermoplastic elastomer(TPE) and polyolefin elastomer(POE) as support materials, PA as PCM and silicon carbide(SiC) as thermal conductivity enhancer. The battery module is displayed in Fig. 18(d). After six high discharge rate cycles of 2.5C at an extreme ambient temperature of 40℃, the maximum temperature and average temperature difference of the battery module laminated with PCM were 56℃ and 3.9℃, respectively. Meanwhile, the material tests indicated that the flexibility and chemistry of the PCM were still better at the low temperature of -40℃. Zhang et al.[165]made new flexible PCMs from four materials, namely, silicone rubber (SR), boron nitride(BN), EG and PA, and evaluated the collision resistance of the PCM with the battery. It was demonstrated that this PCM was able to achieve temperature control while reducing the stresses in the shell and core of the battery during collision by 96.3% and 41.9%, respectively. Yang et al. [166] designed a flexible PCM composed of natural rubber latex(NR), EG and PA. The application of natural rubber not only improved the shape stability of the PCM, but also made the PCM obtain a high resistivity of 2700 (Ω· cm). The BTMS based on this PCM not only maintains the battery temperature but also reduces the risk of short circuit.

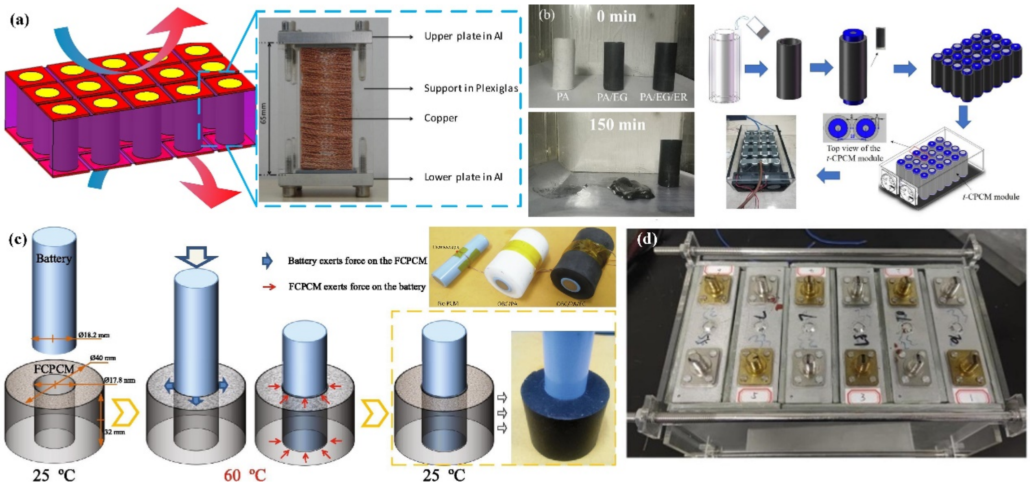

Fig.18 PCM-based thermal management for batteries:(a) Insert copper dutch braided PCM cooling[148], (b) Composite PCM with high mechanical properties[158], (c) Flexible composite PCM[161], (d) Flexible PCM with heat transfer enhancement[164].

Table 5 summarizes the relevant applications of organic PCM in BTMS. PA has become the most popular PCM in BTMS because of excellent thermal properties and economy, and a lot of research work has also been carried out to improve the defects of leaking, weak mechanical properties, and especially thermal conductivity. There is no doubt that the optimization of these properties contributes to the temperature control capability of BTMS, but the specificity related to accident safety, such as volume resistivity and flame-retardant properties of PCM, still lacks attention. Although EG is considered a combustion-suppressing additive, it can accelerate the propagation of thermal runaway[167]. Hence a wider discussion with the evaluation of PCM performance in short circuit, combustion hazards is also required.

Table 5 Summary of BTMS performance based on organic PCMs

Ref.	Li-ion Battery	Battery load	PCM	Melting temperature[°C]	Ambient temperature[°C]	Cooling method	T_{max}[°C]	△T [°C]	Key findings
[140]	2.6Ah, Cylindrical [4 cells]	4C	RT-56	56	22	Forced air cooling	<40	<3.6	Active mode is superior to that under the passive mode
[144]	Pouch, [1 cell]	2C(63970W/m^3)	Capric acid	31.85	21	Natural air cooling	32.1	0.97	Difficult to achieve cooling requirements in 50°C desert conditions
[148]	Cylindrical, [1 cell]	2.45W	PA	35	27	Forced air cooling with copper dutch	<47	<2	Copper dutch has greatly influenced the evolution of the temperature
[151]	2.6Ah, Cylindrical, [1 cell]	Overcharge	PA/EG	37	21	Natural air cooling	42.38	/	PCMs can effectively reduce the battery surface temperature as well as the probability of thermal runaway.
[152]	1.5Ah, Cylindrical, [1 cell]	3C	RT 42 /Al_2O_3	42	35	Natural air cooling	42.77	/	The increase in nanoparticle mass fraction leads to an increase in cell temperature because of the reduction in latent heat.
[155]	38120, Cylindrical, [16	3C	PA/EG/ graphene/	46.1	35	Natural air cooling	41.2	0.8	The new PCM has almost the same local heat transfer as copper foam/PCM, but with

	cells]		carbon nanotubes						less weight and cost.
[156]	1.1 Ah, Cylindrical, [30 cells]	3C	/	/	45~48	Air cooling	59.03	3.65	AlN enhanced PCM has good insulation and battery temperature control
			PA/EG/AlN	50.6	45~48	Air cooling	49.43	0.37	
[158]	1.5Ah, Cylindrical, [24 cells]	1-3C	PA/EG/ER	45.6	40	Forced air cooling	47.2	1	Flexible assembly of tubular PCM saves 54% of PCM amount
[162]	16Ah, Prismatic, [6 cells]	5C	PA/EG/SBS	47.7	30	Air cooling	46	<4	SBS can effectively improve the flexibility and elastic properties of PCM.
[164]	33Ah, Prismatic, [6 cells]	2.5C	/	/	40	Forced air cooling	58.2	5.8	Flexible PCM has good thermal stability and physical properties at extreme ambient temperatures.
			PA/SiC/TPE /POE	40.8	40	Natural air cooling	56	3.9	
[166]	2.6 Ah, Cylindrical, [4 cells]	3C	PA/EG/NR	42.19-43.02	25	Natural air cooling	<45	<2	PCM has good temperature control properties based on high resistivity and flexibility

5.2 Inorganic PCMs

Inorganic PCMs are mainly generated from substances of two types of inorganic molecules, salt hydrates and metallics. Compared with organic PCMs, the heat transfer coefficient is higher and the latent heat exceeds 220 kJ/kg, while the melting temperature range is suitable for the temperature requirements of the battery[168]. Furthermore, inorganic PCMs are non-flammable compared to organic PCMs, which contributes to the safety of the thermal management system. However, this type of material is limited by the following aspects: (1) the compatibility of PCM with metal containers is poor and corrosion will occur; (2) salt hydrates can sub-cool[169] and phase separation[170] leading to poor heat transfer performance; (3) metallics are expensive, over twice as much as PA[24].

Presently there are certain ways to solve the individual defects of salt hydrate PCMs separately, but no holistic solution to all problems is available for this purpose. Therefore, few studies have applied salt hydrate PCMs to the thermal management of batteries. Qi et al.[171] designed the cylindrical 18650 pack to be immersed in $CaCl_2 \cdot 6H_2O$ PCM, with fins assembled on the battery surface to enhance heat transfer. It can be seen that the fin spacing, height and width are all factors influencing the heat dissipation of the battery, and increasing the fin height has the greatest effect on the amount of liquid in the PCM and the battery temperature, which is an effective means to reduce the battery temperature. Ling et al. [172] addressed the need for battery preheating in cold environments by using PCM subcooling to control the storage and release of heat to achieve passive battery preheating. A $CaCl_2 \cdot 6H_2O$- carboxymethyl cellulose (CMC) PCM was formulated and the PCM (with 0.5 wt% of CMC) was stable in the subcooled state at 5°C. When the battery needs to be preheated, the designed device was used to increase the local pressure to trigger the solidification of PCM, and the heating of the battery at 7.5°C/min is achieved. Microencapsulated PCMs are a way to prevent dehydration of inorganic salt PCMs, but the shell increases the thermal resistance, resulting in reduced heat transfer performance, and the process is quite complex and difficult to commercialize. Ling et al.[173]first used EG as a microscopic support matrix, followed by a thin layer of silicone sealant to form a multiscale encapsulation method for macroscopic encapsulation to make sodium acetate trihydrate (SAT)-Urea/EG composite PCM, as demonstrated in Fig.19. The new type PCM has good stability with a phase change temperature change of only 1.7℃ over 100 thermal cycles. In the heat dissipation experiment, it can control the temperature of a pack with a capacity of 20 batteries below 52.3℃, and the maximum temperature difference is less than 4°C, which is better than the PA-PCM with the same melting point. Alqaed et al.[174] wrapped triangularly arranged battery pack with graphene nanoparticles of $CaCl_2·6H_2O$ PCM and analyzed the effect brought by the internal fin structure. The length of the fins increases the PCM merging and freezing process.

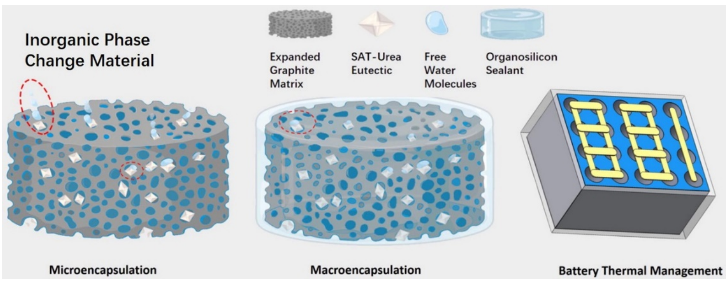

Fig.19 Multi-scale encapsulated inorganic PCM and battery pack system[173].

Similar to salt hydrate PCMs, metallic PCMs need to face the same disadvantages in applications, despite higher thermal conductivity, which can be up to 10 or 100 times higher than other PCMs. For ambient conditions (less than 100°C), low-temperature metallic PCMs including gallium (Ga) and its related alloys, bismuth-based alloys, tin-based alloys, and indium-based alloys have been used in thermal management of electronic devices[175, 176]. The bismuth (Bi), lead (PB), indium (In), tin (Sn), and cadmium (Cd) are also considered to have potential applications[138]. In the area of battery thermal management, Alipanah et al.[177] investigated the difference of pure octadecane, pure Ga and octadecane aluminum foam composites on the thermal management of the battery using numerical simulation. The high thermal diffusion coefficient of gallium and the low Stefan number (longer melting time) result in a slower temperature rise at the battery surface. Even gallium as one component of the composite PCM allows the material to store battery heat more efficiently.

The study of inorganic PCM reflects its good combustion safety, but a more comprehensive analysis of their thermal stability and heat dissipation properties for battery thermal management is still needed. In addition, more accurate thermal models of inorganic PCMs need to be developed to understand the heat transfer mechanism of inorganic PCMs for battery transient heat generation.

5.3 Eutectic PCMs

Eutectic PCMs are formed by combining different materials in specific proportions to form crystalline mixtures of components during the crystallization process. Depending on the type of material combination, it is usually classified as: organic-organic, inorganic-organic, organic-inorganic. Eutectic mixtures can have higher melting points as well as latent heats, but also have similar properties to organic and inorganic materials, with defects of inhomogeneous expansion, which affect the performance of the material in applications.

At present, there are few attempts of eutectic PCM in the field of EVs. Sun et al.[178] configured a eutectic PCM to address the capacity loss of EV batteries in cold environments. Also based on the idea of PCM subcooling to control the heat release, the PCM is mainly composed of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$, STP), sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$, SAT) and deionized water, with a subcooling degree of over 61°C. The combination of this PCM with a power battery effectively increases the electrical energy release of the battery under cold (-20°C) conditions by 6.8%.

Table 6 compiles the relevant studies on inorganic PCM and eutectic PCM. The studies of these PCM only conduct a partial discussion of BTMS applications, mainly including the use of PCM subcooling to achieve preheating of batteries. Therefore, the performance of these PCMs can still be further developed and expanded in the future, or a hybrid design with organic PCMs in BTMS to increase the applicability of PCMs by performing different functions can also be a direction to be explored.

Table 6 Summary of BTMS performance based on PCMs

Ref.	Li-ion Battery	Battery load	PCM	Melting temperature[°C]	Ambient temperature[°C]	Cooling method	T_{max}[°C]	△T [°C]	Key findings
[171]	18650, Cylindrical, [1 cell]	/	$CaCl_2.6H_2O$	29	/	(h=10W·m^{-2}·K^{-1})	≈51.8	/	Improved thermal performance through fin optimization
[172]	3.2Ah, Cylindrical, [1 cell]	1C	$CaCl_2.6H_2O$ /CMC	25-30	5	/	/	/	The PCM preheats the battery at a rate of 7.5 °C per minute to raise the battery from low to room temperature.
[173]	18650, Cylindrical, [20 cells]	2C	SAT-Urea/EG	49.1	25	/	<52.3	<4	The PCM is non-flammable and offers advantages in price and cooling performance
			PA/EG	48.9			57.1	6.1	
[177]	800W/m^2		Gallium	29	28	/	59.1	/	Gallium as PCM makes the battery surface temperature uniform and the discharge time 4.7 times longer.
			Octadecane	28	28	/	60.5	/	
[178]	3.2Ah, Cylindrical, [18 cells]	2C	STP/SAT/ Deionized water	41.1	0	/	/	/	PCM increases the discharge capacity of the battery module

6. BTMS with hybrid technology

6.1 PCM and Heat pipes coupled

Zhao et al.[179] experimentally tested the battery temperature under three forms of thermal management: air cooling, PCM packaging and PCM/heat pipe packaging, with the structure illustrated in Fig. 20(a), and the PCM shell can reduce the maximum temperature difference of the batteries by 33.6%. The insertion of heat pipes into the PCM distributed the heat more evenly, further reducing the maximum temperature difference by 28.9%. Although the final temperature difference gradually increases with time, the combination of heat pipe and PCM still manages to keep the battery pack temperature difference below 5°C for the longest time. Wang et al.[180] fills the PCM into a copper tube load with fins, arranged alternately with an aluminum heat pipe in the 18650 cylindrical battery gap. The experimental results show that the effect of the heat pipe is to reduce the battery temperature rise, while the PCM tube is to reduce the temperature difference within the battery module. Peng et al.[181] further modeled and analyzed the melting process of PCM and the thermal performance of the battery based on the design of this system. By adding a specific percentage of graphite to the PA, the heat absorption of the PCM is enhanced, which helps to optimize the final temperature of the battery. However, it should be noted that the uniformity of PCM melting is significant for the temperature difference of the battery pack and is a factor to be concerned.

The heat pipe is also made into an L-shape to reduce the space in which the heat pipe extends, although this may reduce the heat transfer capacity of the heat pipe.

Wu's study[182] also determined that the PCM improved temperature uniformity, and the placement of the L-shaped heat pipe further reduced the battery temperature, especially on the condensing side of the heat pipe. The most important role of the heat pipe is to ensure the initial temperature of the PCM for each cycle, so that the PCM can phase change at its proper temperature. Putra et al.[183] investigated the thermal management performance of the L-shaped heat pipe against gravity. In this installation form, the internal liquid of the heat pipe has to overcome the gravitational backflow, so the heat transfer capability is usually decreased. However, it can be observed that the battery temperature is only 31.9℃ at 60W. The PCM absorbs part of the heat from the battery to enhance the effect of the heat pipe, while the heat pipe effectively exports the heat to enhance the heat absorption rate of the PCM. Because of the mutual promotion of both makes the combination of heat pipe and PCM has better performance than heat pipe alone. Yi et al.[184] used a combination of orthogonal test and fuzzy correlation analysis to evaluate the influencing factors on the maximum temperature and temperature difference of the battery pack. The maximum influencing factors of the two temperature parameters are different, because the temperature of the battery pack is most likely to be influenced by the coolant flow rate, while the temperature difference of the battery pack is determined by the liquid cooling tube inlet diameter. Jiang et al.[185] sandwiched the flattened heat pipe between the PCM and the battery, and the heat transfer of the flattened heat pipe to ensure the latent heat recovery of the PCM, maintaining the long-term effectiveness of the thermal management performance of the battery module. Given the influence of factors such as heat pipe and PCM heat dissipation competition during the cycle, the study also gives recommendations for the selection of PCM melting point and condenser heat transfer performance for this system. Karimi et al.[186]tried to completely submerge the heat pipe in the PCM, and the battery temperature dropped significantly compared to the cooling form of heat pipe alone. Zhang et al.[187] builds the BTMS with another idea, which consists of a flattened heat pipe to transfer the battery heat to the PCM, and a fan to assist in heat dissipation, as described in Fig. 20(b). This design is to improve the thermal resistance in the heat transfer path, effectively releasing the latent heat of the PCM and improving the performance of the battery pack for long cycles. Zhang et al.[188] designed a thermal management system combining PCM, heat pipe and liquid cooling, as shown in Fig. 20(c), and constructed a model of the system using the adaptive kriging-high dimensional model representation method for sensitivity analysis of influencing factors and optimal design. Leng et al [189] analyzed the heat flux distribution inside the coupled system based on a mathematical model to obtain the heat transfer mechanism in each stage. The system energy saving is achieved through multi-objective optimization for BTMS improvement, and the energy saving rate can reach 71.06% at the worst operating condition[190].

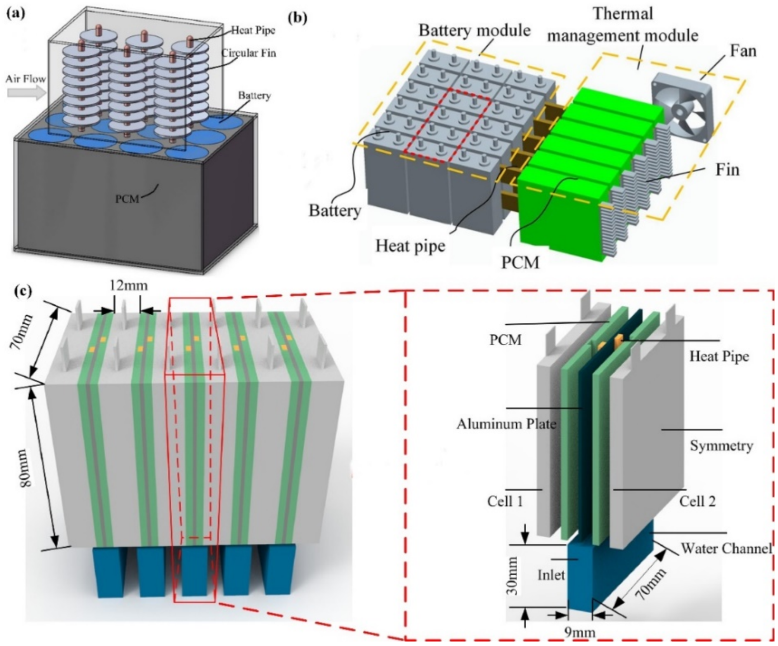

Fig. 20 Thermal management system combining PCM and heat pipe: (a)PCM and battery attachment combined with air cooling[179]; (b) Heat pipe and battery attachment combined with air cooling[187]; (c) PCM and battery attachment combined with liquid cooling[188].

Flat heat pipes are also available for combination with PCM. Huang et al.[191] placed the aluminum flat heat pipe with PCM completely, and the heat pipe was filled with ethanol, while the aluminum shell without phase change medium was used as a reference. The comparison shows that the flat heat pipe can keep the battery pack at the set temperature for a longer period of time, and the temperature difference of the battery pack is less than 1°C under long cycle conditions. Hu's research[192]indicates that the presence of PCM in the heat pipe system helps to eliminate the "cold start" phenomenon at low power conditions, and the battery temperature is more averaged. At the end of 3C discharge cycle, the PCM coupled with the flat heat pipe system can transfer 94% of the battery's heat. Chen et al.[193] conducted a study on the optimization of the combination of flat heat pipe and PCM, and concluded that the melting temperature of PCM should be lower than the starting temperature of heat pipe, so that the temperature difference of the battery pack can be optimized. The optimization strategy is also developed for the PCM thickness in the system and is effective when the convection conditions and heat pipe heat transfer coefficient are small. As can be seen the combination of the heat pipe and PCM effectively improves the performance of the battery pack at maximum temperatures and temperature differences, and the heat pipe extends the melting time of the PCM, the two compensate for mutual disadvantages.

6.2 Heat pipes and two-phase coolant cooling coupled

As mentioned in Chapter 3, refrigerant cooling has been effective in automotive systems, but further refinement is still needed. Immersion cooling, although excellent in cooling, does not yet have a viable solution to achieve sustainability and circulation of boiling liquids. As for the cold plate-based indirect cooling, the pressure drop of refrigerant caused by microchannels still creates a large burden on the system. Therefore some scholars add heat pipes for heat transfer between the battery and the direct evaporation unit to solve the above problems. Liang et al.[194] arranged the batteries in series on the steel plate and combined with the evaporating secion of the partially flattened heat pipe, while the condensing end of the heat pipe is welded into the R141b refrigerant channel, thus forming a complete battery pack design. The experiments identified the refrigerant flow rate as an important influencing factor. When the refrigerant flow rate increased, the maximum temperature of the battery tended to decrease and then increase, which was most likely due to the shortening of the refrigerant superheating time, and thus boiling was more difficult. And the comparison results between single-phase cooling and boiling cooling proved that boiling cooling can get better temperature uniformity and requires less flow rate.

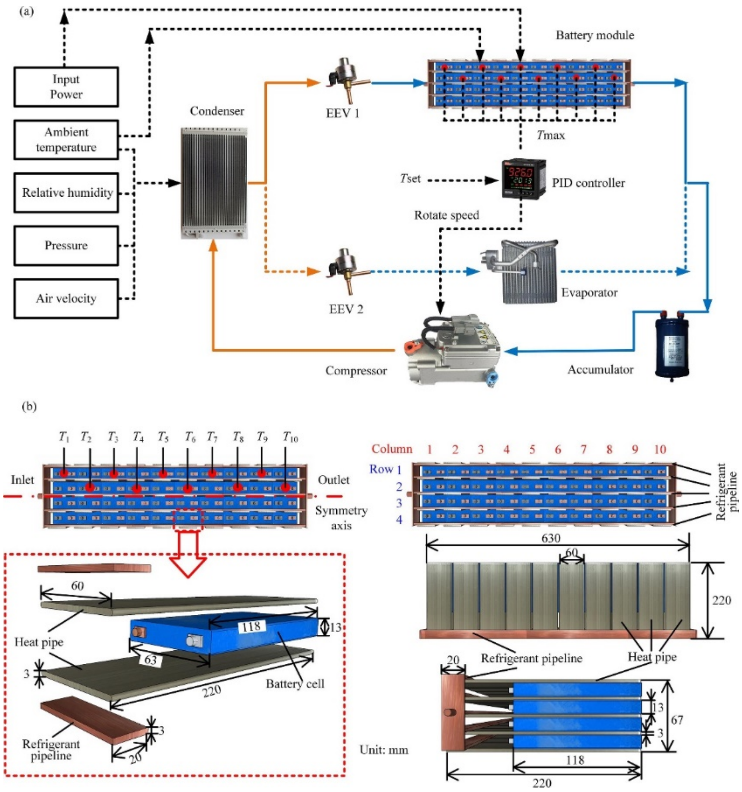

Fig. 21 BTMS based on heat pipe and direct cooling coupling[195]: (a) Structure of BTMS; (b) Battery module.

Yao et al.[195] investigated the combination of heat pipe and air conditioning system for refrigerant cooling of the battery module, as shown in Fig. 21. The study analyzed the influence of system preset temperature and heat production with the battery, and it can be concluded that the increase of preset temperature can improve the energy efficiency and exergy efficiency of BTMS. Meanwhile the excessive superheat of the refrigerant outlet is pointed out to be the main cause of the temperature difference of the battery. Zhou et al[196] made improvements for submerged cooled battery packs, where the immerged battery pack is in a completely confined space and the vaporized coolant (Novec 649) is cooled down by heat pipes to bring it to condensation. During normal charging and discharging, the maximum temperature of the battery can be maintained at 47°C or below. Changing the airspeed at the condensing section of the heat pipe can adjust the boiling and non-boiling state of the submerged cooling, thus playing an active role in control.

The intersection of two-phase technologies is to capitalize on the performance advantages of each technology to compensate for obtaining beneficial integrated heat transfer, where the combined use of the high heat transfer of heat pipes and the uniform temperature capability of phase change materials is more widely discussed at present. The summary of several hybrid BTMS studies in Table 7 indicates that the hybrid of technologies can bring about the improvement of system heat transfer capability, but the limitations of PCM types involved at present, and the majority of heat pipes used are conventional heat pipes. Efficient heat transfer of two-phase coolant is used in combination with heat pipes to enhance the heat transfer performance of heat pipes, while the flow channel design of the system can be simplified and energy consumption can be reduced. However, little research has been done on this type of system and needs to be expanded.

Table 7 Summary of hybrid BTMS performance

Ref.	Li-ion Battery	Battery load	PCM	Heat pipe	Ambient temperature[°C]	Cooling method	T_{max}[°C]	△T [°C]	Key findings
[181]	3.2Ah, Cylindrical, [40 cells]	2C	PA/EG	Typical	25	Forced air cooling with fins	44.65	3.77	Uniform melting of PCM leads to increased temperature difference
[182]	12Ah, Prismatic, [5 cells]	5C	/	/	20	Nature air cooling	63.1	2.6	Extended run time for heat pipe assisted PCM BTMS
			PA/EG	/			53.2	2	
			PA/EG	Flattened (L-shape)			50.9	1.8	
[188]	25Ah, Prismatic, [5 cells]	5C	PA/EG	Flattened (ultra-thin)	25	Liquid plate with aluminum plate	36	1.7	Established BTMS and optimization methods for the combination of liquid cooling, heat pipe and PCM
[191]	1.1 Ah, Cylindrical, [30 cells]	3C	PA/EG	/	35	/	45.56	1.75	Liquid-cooled, heat-pipe and PCM-coupled BTMS stays at the target temperature longer in the cycle
			PA/EG	Flat		Air	44.94	1.46	
			PA/EG	Flat		Liquid	43.84	1.47	
[195]	7Ah, Prismatic, [40 cells]	40W	/	Flattened (ultra-thin)	25, 30, 35	Cooling plate(R134a)	/	<3	Discussed the cooling strategy and system energy efficiency
[196]	60Ah, Prismatic, [14 cells]	2C	/	Typical	/	Liquid immersion (Novec 649)	48	2	Demonstrates better thermal performance and lower energy consumption

7. Discussion

7.1 Current limitation and challenges

In response to the battery thermal issues brought about by the development of battery energy density and fast charging, technologies based on the principle of phase change process are integrated into conventional BTMS to improve the thermal management capability of BTMS and achieve technological innovation. Such techniques include two-phase coolant cooling and heat pipe technology based on evaporation/boiling and condensation of the medium, and PCMs based on melting and solidification processes of the material. Despite the differences in working medium and technology specifications, the above findings have confirmed a similar result that the phase change technology can have an enhancing effect on battery operation, allowing the battery to operate at higher charge and discharge rates and in the desired temperature range. Table 8 summarizes the characteristics of some specific technology solutions to show the differences between each technology.

Table 8 Comparison of phase change technology based BTMS methods in EVs

Technology	Technical method	Advantages	Disadvantages	Ref.
Two-phase coolant cooling	Refrigerant cooling plate	Simplified components; Good temperature drop	Leakage, Poor temperature difference	[64]
	Fuel immersion	Simplified components, Good temperature drop	Leakage, Combustibility, Influenced by liquid level, Short circuit risk,	[87]
Heat pipe cooling	Partially flattened heat pipe with liquid	Dependable; Good temperature drop	Complex structure, Large volume	[102]

	cooling			
	Micro heat pipe arrays with forced air cooling	Weight light; Dependable; Good temperature drop	High cost Low heat transfer limit	[113]
PCM cooling	Organic PCM with air cooling	Flexibility Weight light; Good uniform temperature	Combustibility, Short circuit risk, Low thermal conductivity	[162]
	Inorganic PCM with air cooling	Non-combustible Preheat control Good uniform temperature	Poor compatibility, Short circuit risk,	[173]
Heat pipe/PCM	Flat heat pipe with PCM	Good temperature drop, Good uniform temperature,	Complex structure, Large volume, Combustibility	[191]
Heat pipe/ Two-phase coolant cooling	Typical heat pipe with two-phase coolant	Good temperature drop, Good uniform temperature,	Complex structure, High weight	[196]

Compared to PCM cooling and heat pipe cooling, two-phase coolant cooling is the first to be applied to existing EV models in the form of indirect cooling because of its simplification and economic improvement of the traditional BTMS. The present stage of research has clarified that the coolant inlet conditions of the two-phase coolant cooling thermal management system, including the coolant temperature, pressure and flow rate, are the key factors in controlling the battery pack temperature, as it is important to ensure that the coolant is in a two-phase flow state. However, considering the linkage between the cooling system and the air conditioning or fuel system in the vehicle, it is not possible to adjust the coolant conditions singularly for the battery pack temperature and ignore the performance and efficiency of other systems. Therefore, an effective control strategy is still needed to evaluate the status of each system and adjust the coolant conditions of BTMS in real-time to respond to load changes, thus ensuring the operational performance of the whole vehicle. Another issue that needs to be clarified is the selection of the two-phase coolant, especially for the refrigerant. Most of the refrigerant types currently explored have a high GWP, which is not compatible with environmental requirements under the pressing global warming issue. Therefore, the refrigerants used in AC systems may have to meet the 0 ODP and GWP (<150) limits, while the refrigerants discussed so far are likely to be restricted and banned in the future[197].

The heat pipe, based on the same principle of vapor-liquid phase change, is mainly affected by the external thermal and cooling conditions after machining, which is also similar to PCM. Therefore, the BTMS using PCM and heat pipe is usually designed to combine with traditional air and liquid cooling, so as to achieve efficient cooling. In other words, heat pipes and PCM can be considered as additional components to the conventional thermal management system, which also indicates an increase in system weight and space, especially when systems are designed with longer condensing sections of heat pipes or with a large number of metal fins and heat conducting elements to enhance heat transfer. This is a point that has been ignored in many studies and has led to the design of PCM/heat pipe systems that deviate from the actual requirements, such as the inclusion of thicker PCM in the battery to achieve better heat dissipation, or the obvious practical disadvantages of the system structure. Therefore, there is still a necessity to establish a more comprehensive evaluation mechanism to assess the performance of new phase change systems. In the development of EV thermal management requirements, the gap between the battery will become as small as possible, so the application of heat pipes and PCM will also develop to a thinner scale, which puts demanding requirements on the design and synthesis of both itself. It is worth mentioning that the current application of PCM is more discussed for the ability of battery temperature equalization, while PCM has not been able to provide long-term operational capability[198]. However, the authors would like to highlight that the real advantage of the PCM is the thermal storage capacity, which cannot be actively achieved by components such as heat pipes. The thermal storage of the PCM can be applied to preheat the battery and actively adjust the coolant temperature, thus reducing the energy consumption of the battery system, but the related application modes are less explored whether in PCM or hybrid heat pipe and PCM systems.

The three technologies also face the same development problems. Both battery performance and phase change heat transfer are responsive to changes in temperature, so both influence each other in the heat transfer process and show a coupling relationship. Theoretical models and numerical simulations are effective methods to quantify heat transfer and are commonly used in BTMS research. However, most of the phase change heat transfer is coupled in a simplified form in the numerical simulations of BTMS. For example, the heat pipe in the simulation is mostly characterized by the effective thermal conductivity or a simple thermal resistance network, but this cannot reflect the effects of heat source distribution, heat input inhomogeneity, cooling variations, and other factors on the heat transfer of the heat pipe. While the heat production of the battery will vary in real time with SOC, temperature, which is especially complicated in the case of variable C-rate, such coupling relationship is not clear in the current study. Therefore, it is still necessary to develop a battery thermal model that can characterize the heat transfer process of phase change technology, analyze the heat transfer mechanism between the battery and phase change solutions, such as PCM, heat pipe, and quantify the heat transfer process. Further, accurate simplified models are developed for the performance study of the whole battery module and battery pack.

Although the cooling conditions, such as temperature and flow rate, have been explored in the study of BTMS with two-phase transformation to influence the system performance, the aim is to determine the effective range of BTMS operation, while ignoring the controllability of BTMS[64, 96, 118, 193]. Providing a cooling cycle in the BTMS enhances the upper limit of system control and also provides the system with the ability to make active adjustments. It has been found that increasing the flow rate and lowering the circulating medium temperature can slow down the battery heating, but it also introduces a larger power consumption of the devices. Since the purpose of BTMS is to control the temperature within a threshold rather than constant, in general the cooling cycle does not need to be maintained at high power consumption conditions at all times, as confirmed by the intermittent cooling scheme[101]. Therefore, the control strategy of BTMS is worth exploring and is important for the energy efficiency improvement of the system. In addition, combined with battery SOC and SOH monitoring and pre-charge model prediction, the development of control strategies can also reduce the safety risk of the battery[199].

Another key point worth discussing is the security of BTMS. As such, two-phase cooling coolants such as fuels, hydrocarbon refrigerants, and mainstream PA PCMs carry a risk of combustion. The relevant studies in refrigerants specify a minimized amount of flammable refrigerants[200]. And even relatively safe heat pipes have heat transfer limits[201], meaning that a maximum heat transfer limit or heat transfer failure exists, and the impact of these additional factors is to be considered in the design of the BTMS.

7.2 Future research direction

After reviewing the various BTMS technologies for the utilization of latent heat of phase change in EV and considering the current bottlenecks of the technology and practical needs, the following highlights still need continuous attention in the future to improve the technical capabilities of BTMS:

- Two-phase coolant cooling technology is integrated with the original system of the vehicle, using boiling heat transfer to optimize battery temperature. In general, the operating parameters of the coolant are still the key to the effectiveness of the battery temperature control. Since this type of system is a multi-system coupling of the vehicle, effective dynamic control strategies are required to regulate the operating parameters of the coolant following the discharge of the battery and the load changes of the passenger compartment and other systems. Data-driven and machine-learning approaches are means to solve such multifactorial problems, and the approach has been applied to the optimization of liquid cooling systems[202]. In this way, more effective diagnosis of the state of each system and prediction of the system operation are facilitated to give a better control strategy. In addition, the selection of coolants should pay more attention to the requirements of environmental protection, such as refrigerants can choose hydrocarbons (HCs), Hydrofluorocarbons (HFCs), Hydrofluoroolefins (HFOs) and other low GWP working medium, but the safety factor should also be fully considered[203, 204].

- Under the trend of compact battery system, the heat pipe will also be limited to ultra-thin scale, and the performance will be more sensitive to the transient heat generation of the battery and the change of external cooling conditions. For battery systems, more attention needs to be paid to the design of the internal structure of the heat pipe and the integral arrangement of the heat pipe in the system to improve the starting characteristics of the heat pipe under battery heat release and the heat transfer characteristics under stable operating conditions. Meanwhile, it is also necessary to focus on the system performance exploration when the heat pipe reaches the heat transfer limit. Compared with the copper-water heat pipes commonly adopted, heat pipes made of aluminum shells are expected to be further developed due to their lightweight.
- PCM can effectively improve the temperature uniformity of the battery, while the development of composite PCM strengthens the mechanical properties and improves the applicability. However, the safety issues arising from the flammability and conductivity of PCM still need to be concerned, especially since PA is the main PCM currently developed. Meanwhile, controllable heat

storage/release mode and system design of PCMs need to be further explored, which can help further improve the temperature control capability of BTMS as well as the development of energy saving methods.

- PCM/heat pipe and hybrid BTMS can take full advantage of phase change process to optimize the battery temperature at high charge rate. As to ensure the practical value of the designed thermal management system, the evaluation of the system energy density, size and other indicators can provide a more comprehensive reference and guidance for the EV industry while analyzing the thermal performance of the thermal management system.
- Phase change based BTMS systems require enhanced model development to describe the linkage and influence relationship between the thermoelectric chemical behavior of the battery and the phase transition heat performance to describe accurately the effect of complex operating conditions such as EV dynamic loading and cooling conditions on the battery pack. And the BTMS can be diagnosed and dynamically adjusted to achieve safe and energy-efficient operation in combination with control strategies.

8. Conclusions

The future of EVs will drive performance improvements such as range and fast charging, thus requiring BTMSs with high energy density, low energy consumption and high efficiency which has led to the introduction of efficient heat transfer technologies that utilize the latent heat of phase change. Although the employed EVs in the market have not been perfectly realized, this review, by classifying and summarizing the development of phase change technologies now introduced in EVs, confirms that both two-phase coolant cooling and heat pipe technologies based on vapor-liquid phase change and PCM technologies with liquid-solid phase change contribute to improve the heat transfer performance of conventional BTMS. And the hybrid systems have a more reliable performance because of the mutual refinement between the technologies. However, the economics, environmental friendliness, safety, and adaptability to changing operating conditions of the new systems still deserve attention. In order to achieve mature commercial applications, these new phase change based thermal management technologies still need further development of practical system architectures, corresponding control strategies and fuller system evaluation criteria.

CRediT authorship contribution statement

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Yuying Yan: Resources.

Yong Li: Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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