

Thermal management technology of power lithium-ion batteries based on the phase transition of materials: A review

Kun Jiang^{a,b}, Gaoliang Liao^{a,b,*}, Jiaqiang E^{a,b}, Feng Zhang^{a,b}, Jingwei Chen^{a,b}, Erwei Leng^{a,b}

^a College of Mechanical and Vehicle Engineering, Hunan University, Changsha 410082, China

^b Institute of New Energy and Energy-saving & Emission-reduction Technology, Hunan University, Changsha 410082, China



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ABSTRACT

With the rapid development of electric vehicles and hybrid electric vehicles industry, heat generation problem of vehicles power source has been becoming a challenge which influences the temperature distribution and lifespan of batteries. An efficient battery thermal management system for controlling the temperature of batteries in a reasonable range and improving battery module's temperature uniformity to optimize the performance of power lithium-ion (Li-ion) batteries is necessary. In recent years, phase change material (PCM) is widely used as the working medium of battery thermal management system, which is an effective method to control the working temperature of batteries. In this context, this paper reviews two types of battery thermal management systems (BTMS) based on phase transition principle, including the thermal management system based on solid-liquid phase transition principle and the thermal management system based on liquid-gas phase transition principle. In addition, for the prediction of battery heat generation, several kinds of existing thermophysical models are reviewed in detail. These thermophysical models can accurately predict the distribution of heating area and the rising trend of temperature, which can provide thought support for the development and construction of thermal management system or model, as well as provide theoretical basis for the established thermal management system. Furthermore, the simulation time and calculation error of various models in computer are also summarized and discussed in this paper. On the other hand, the advantages, disadvantages and cost-effectiveness of each battery cooling technology are evaluated and discussed objectively in the latter section of the paper. In view of the shortcomings of some technologies, this paper discusses and puts forward appropriate optimization measures to provide a reasonable solution for the further research of battery thermal management system in the future.

1. Introduction

As the fossil fuels (e.g. oil) consumption rapidly rising for the past few years, the limited availability of fossil fuels is dwindling. In addition, the greenhouse gases and pollutants emitted by the energy consumption of the transportation industry such as carbon dioxide, dust, sulfide and nitrogen oxide seriously cause Global warming and human disease [1]. Under the double pressure of environmental problems and energy crisis, almost all countries in the world have been paying attention to make strategies of energy development as well as developing new energy and renewable energy for the purpose of energy conservation and environmental protection [2,3]. In order to inhibit the production of pollutants and achieve the purpose of zero emissions, clean energy vehicles have obtained the fast development in recent years. Clean energy vehicles, including pure electric vehicles (EV),

hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV), have proven to be more energy-efficient and environment friendly than the traditional internal combustion engine systems [4,5]. Some Chinese scholars estimated that by 2030, if fuel economy reaches Japan's present level and clean energy vehicles attains 50% of the market share in China, China's transport could probably realize 42% energy saving in vehicle fuel consumption [6,7] which would greatly decrease the emission of greenhouse gases.

Owing to the high energy density, low self-discharge and long cycle life, lithium-ion battery (LIB) as a suitable power source has been paid much attention [8–10]. However, the beginning of developing the new field has never been easy. Heat generation issue of batteries is an important bottleneck restricting the development of electric vehicle technology. The heat generated by the battery during operation mainly comes from the electro-chemical reaction and the resistance of electron

* Corresponding author.

E-mail address: [liaogaoliang@hnu.edu.cn](mailto:liao.gaoliang@hnu.edu.cn) (G. Liao).

conduction inside the battery. The electro-chemical reactions of batteries during charging and discharging process can only happen in a certain temperature range which means that the working temperature of lithium-ion battery should stay within limits.

The power performance of electric vehicles is deeply influenced by battery pack performance of which controlling thermal behavior of batteries is essential and necessary [12]. Studies have shown that lithium ion batteries must work within a strict temperature range (20–55°C), and operating out of this temperature range can cause severe problems to the battery. In addition, the temperature difference among all cells could not exceed 5 °C [13,14]. If the working temperature of batteries does not meet above strict temperature range or temperature difference of single battery cells in battery modules exceed 5°C, the performance of the batteries will be seriously affected. Firstly, if the temperature of batteries is at a lower level (such as below 0°C), the charging and discharging capacity of them will be reduced and both severe energy and power losses issues will occur [15–18]. Researches [18,19] have shown that batteries have only 10% of its capacity compared to room-temperature condition, as a result, these factors seriously restrict the application of lithium batteries in high altitude, polar regions, aerospace and other cold areas. Recent researches showed that some efficient methods have been put forward to solve above issues, such as adding some auxiliary equipment for heating or insulation [20–22] and changing the composition of electrolyte to decrease freezing point so that preventing freezing and allow Li-ion diffusion [23–25]. Secondly, at a high temperature level, the heat generated by the battery will accumulate rapidly and lead to the thermal runaway of the battery as well as the possibility of battery deflagration more seriously without cooling the batteries or battery modules [84]. In order to make the batteries working in the allowable ambient temperature range, efficient battery thermal management systems should be put forward. In the current studies, three common heat management systems are used to control the thermal dissipation of batteries which are based on air cooling, water cooling and PCMs cooling. Considering the diverse thermal conductivity and convective heat transfer coefficient of working mediums, the three common heat management systems yield different performance. Using air as the heat dissipation medium is that directly making the air through the battery module to achieve the purpose of thermal dissipation. Researches [26–28] have shown that air cooling cannot effectively decrease the temperature of batteries when batteries are at a high temperature level. Therefore, in the case of small power and a friendly ambient temperature, it is very suitable to adopt air-cooling for thermal dissipation from the perspective of cost. Compared with the air-cooling based thermal dissipation, when the output power of the batteries is large or the batteries is in bad working conditions, the liquid-cooling based thermal dissipation could obtain better performance. In some previous researches [29–32], liquid-cooling can significantly weaken the maximum temperature of the batteries surface and reduce temperature difference between batteries. However, there are some auxiliary devices for the liquid-cooling thermal system, such as pumps which make the BTMS more cumbersome and consume additional power [33]. Therefore, thermal dissipation based on liquid-cooling is also not a perfect solution. With the development of recent years, the utilization of PCMs in the BTMS has become a thriving trend due to its prominent advantages: temperature stability, large latent heat, simple structure and low power consumption [34–36]. As one of the most widely used organic PCMs, paraffin with a nearly constant phase change temperature, stability and non-corrosiveness is more suitable for battery thermal management [12,37,38]. However, low thermal conductivity and phase segregation phenomenon make the pure paraffin performance deteriorated. Therefore, pure phase change materials are not sufficient for transferring the heat from battery cells [13]. To improve the performance of pure phase change materials, many studies have done by researchers, such as adding metal additives in paraffin to improve thermal conductivity [9,39–42], using metal fins to couple with phase change materials [43–45], enhancing

CPCMs (composite phase change materials) by metal container [46,47], filling PCMs in graphite to improve thermal conductivity [48–50] and adding carbon fiber or carbon nano-tubes in phase change materials [51–53]. And the results showed that these methods could greatly improve the thermal conductivity and overall performance of PCMs. In addition, the technology of heat pipe cooling [155,156,161] and boiling cooling [171–174] based on the principle of liquid-gas phase transition can also effectively manage the heat generation of batteries. As the heat pipes were difficult to meet the heat dissipation requirements of the batteries under the high heat flux [157,163], the new thermal management system coupled the heat pipes with metal fins and PCM [167,168] were proposed to solve the above problems. Some new working mediums [173,174] in recent studies applied in boiling cooling technology for battery thermal management are also presented in this paper.

Therefore, with the continuous development of BTMS based on phase transition technologies, it is necessary to systematically summarize some existing technologies. In this paper, the thermal management strategies of lithium-ion batteries based on phase change materials were reviewed and consolidate some interesting results recently. Furthermore, this paper also has the following novel points compared with other review papers. In the second section, three basic thermophysical models of lithium-ion batteries are introduced in detail, These thermophysical models can accurately predict the distribution of the heating area and the rising trend of the temperature of the battery cell, which can provide ideological support for the development as well as construction of thermal management system or model, and provide theoretical basis for the established thermal management system. Furthermore, the simulation time and calculation error of various models in computer are also summarized and discussed in this section. In the third section of the paper, the temperature control characteristics in the process of phase transition are introduced in detail from the perspective of thermodynamics. Until now, inorganic phase change materials, hydrate phase change materials and PCM capsules are rarely used in battery thermal management. The feasibility of their application is also analyzed and discussed. For the composite components in the enhanced phase change materials, most of them have good conductivity, which makes it easy for researchers to ignore the electric leakage of batteries. Some related improvement methods are also introduced in this section. In the fourth section, the working principle of different kinds of heat pipe and its application in battery thermal management system are introduced in detail. In addition, for boiling cooling, this section reviews the existing research from pool boiling and flow boiling in detail. At the end of the paper, the advantages and disadvantages, cost-effectiveness and energy consumption of various technologies are analyzed and discussed in detail. In addition, the paper discusses and puts forward appropriate optimization measures for these technical problems, so as to provide a reasonable solution for the further study of battery thermal management in the future.

2. Li-ion battery heat generation model

2.1. The mathematical model of battery heat generation based on dimensions

The main mathematical models based on dimensions used to study the thermal behavior of batteries include the zero dimension (lumped parameter modeling), one dimension (1D), two dimensions (2D) and three dimensions (3D). Generally speaking, the low-dimensional models can be regarded as a simplification of the three-dimensional model based on the actual situation of the battery. For example, a two-dimensional model can be regarded as a three-dimensional model that is homogeneous in one special dimension. Therefore, the battery behavior in this dimension is the same, which can be ignored during the development of the model and regarded as a two-dimensional model. Readers can refer to the 2D current distribution model in the 3D SEMP

model (Simplified Electrochemical Multi-Particle Model) which is developed by Mastali et al [78]. Other low-dimensional models can be simplified in this way and so on. These low-dimensional models have greatly improved the efficiency of mathematical computation [79] compared with the three-dimensional models before simplification, which is also one of the purposes of model simplification. For the three-dimensional thermal mathematical models of batteries, the establishment of them is generally by the coupling of electric models, electrochemical models and thermal runaway models based on different dimensions and heat generation models based on partial differential equation of heat conduction. Therefore, the thermal mathematical models of batteries are usually obtained by coupling several different models.

2.2. The mathematical model of battery heat generation based on physical mechanisms and types of chemical reactions

According to the types of the physical mechanisms and chemical reactions in the current researches, the battery thermal mathematical model can be divided into electrochemical-thermal model, electro-thermal model and thermal runaway model [92–95].

2.2.1. Electrochemical-thermal model

The electrochemical model widely used in the early stage was the Pseudo Two-Dimensional (P2D) Model [65–68] which was developed and proposed by Newman et al [64]. The P2D model divides the battery cells into the particles domains and electrode domains by establishing a series of partial differential government equations. These equations include the charge conservation equation, the mass conservation equation, the Fick law based on the diffusion theory and the Butler-Volmer equation that connects the particles domains and electrode domains. Then the dependence between the current density and the voltage across the battery active material layer is coupled with the heat source term in the thermal models, which are used to solve the battery temperature distribution. Based on P2D model, Panchal et al. [68] developed an electrochemical thermal model to predict the transient temperature and voltage distribution of the battery at different discharge rates. The results of the discharge experiment in the laboratory were in good agreement with the simulation results. However, it is time-consuming to solve these partial differential equations in numerical simulation.

In current researches, there are two methods to simplify the P2D model. The first method is mathematical order reduction methods and these methods mainly include the Laplace transformation technique [69], the proper orthogonal decomposition [70,71], the polynomial approximation [72], the Galerkin's method combined with the volume average technique [73] and the Pade approximation [74,75]. The second common method is that the mathematical methods couple with physical structure simplification or electrochemical reaction assumptions. By this method we can develop such as the Single-Particle (SP) model [76,96], the Multi-Particle (MP) models [77] and the Simplified Multi-Particle (SMP) model [77]. The key assumption in the single-particle model is that the current distribution is taken to be uniform along the thickness of the porous electrode [76], however the multi-particle model assumes that all of the electrode active material is exposed to the same electronic and ionic environment [78]. The Simplified Electrochemical Multi-Particle (SEMP) [78] model is proposed based on SP model and a common Homogenous Pseudo-two-Dimensional model (HP2D) [79,80] is also developed based on P2D model. Some relevant model assumptions and simplified methods are shown in Fig. 1.

Li et al [77] obtained the SMP model by simplifying the P2D model to verify the accuracy and computational efficiency of the model. Contrast experiments are performed among SMP model, P2D model and other simplified models. What's more, some relevant contrast experiments are also performed between the SMP model and experimental

data. Based on the simulation results, the computational time of the isothermal SMP model is reduced by two orders of magnitude with almost no loss of accuracy. According to a set of battery experimental data at wide range of temperatures (10°C–45°C) and up to 5C-rate galvanostatic and pulse-current operating conditions, the overall maximum Root Mean Squared Error (RMSE) of the thermal SMP model is 22.70 mV, which is acceptable for online applications [77]. Some uncommon methods, such as nondimensionalizing independent variables of equations, can also be referred to. Chu et al. [91] also proposed that nondimensionalizing some of the original independent variables of the original partial differential equations so that these dimensionless variables were used as the new independent variables to reformulate the original partial differential equations of P2D model. Through this novel method, the number of independent variables could be reduced from 36 down to 24 so that the complexity of the equations was simplified to some extent.

2.2.2. Electro-thermal model

There are two main types of electro-thermal models. The first type divides the battery into electrode domain and current collector domain and the electrode domain is between the two current collectors which describes the battery behavior by building an equivalent circuit with multiple RC elements. As a matter of fact, the model is a 2nd-order Thevenin model with a bi-directional structure using a combination of voltage sources, resistors, and capacitors [54,55]. Furthermore, the current distribution on the current collector is described by a 2D current distribution model so that the distribution of current or current density (or other electrical parameters) in the main area of the battery obtained from the above models are coupled with the heat generation model to obtain the temperature distribution of the battery. Shovon Goutam et al [56] proposed an improved 2D potential distribution model based on equivalent circuit model and the constructed equivalent circuit schematic is visible in Fig. 2(a) and (b). In order to simplify the calculation and reduce the input parameters, an analytical method based on empirical solution is introduced.

Furthermore, the comparison of time and accuracy between the electro-thermal model based on the equivalent circuit model and several simplified models under different assumptions is carried out at the end of the paper and the comparison results are shown in Fig. 3. It can be seen from the figure that the original model has the highest accuracy but the longest solution time.

Lin et al [57] also developed a lump-parameter electro-thermal model based on equivalent circuit model. Over a wide range of operating conditions, this computationally efficient mathematical model can predict battery core temperature which is often easily overlooked, SOC (State of Charge), terminal voltage and surface temperature. The proposed parameterization scheme allows separate identification of the electric and thermal sub-models, which greatly reduces the complexity of the parameterization process. Additionally, the parameters of the electric model are temperature dependent so that capturing the temperature close to the electrode assembly (core temperature) can also enhance the accuracy of voltage estimation [57]. Such advantage is desirable especially under high current application where the temperature swing is large and fast [57] which is one of the advantages of the lumped parameter model. Similar studies may refer to works of other researchers [55,58–60].

The other type electro-thermal model is based on data fitting method which assumes that the heat produced by the battery consists of reversible heat and irreversible heat. The expression is as follow:

$$q = I(U_{OCV} - V_{bat}) + IT \frac{dU_{OCV}}{dT} \quad (1)$$

where I is the current, U_{OCV} is the battery open circuit voltage, V_{bat} is the battery voltage. The first term on the right-hand side of Eq. (1) is the irreversible heat including Ohmic resistance heat and polarization resistance heat as well as the second term is reversible heat. Then the

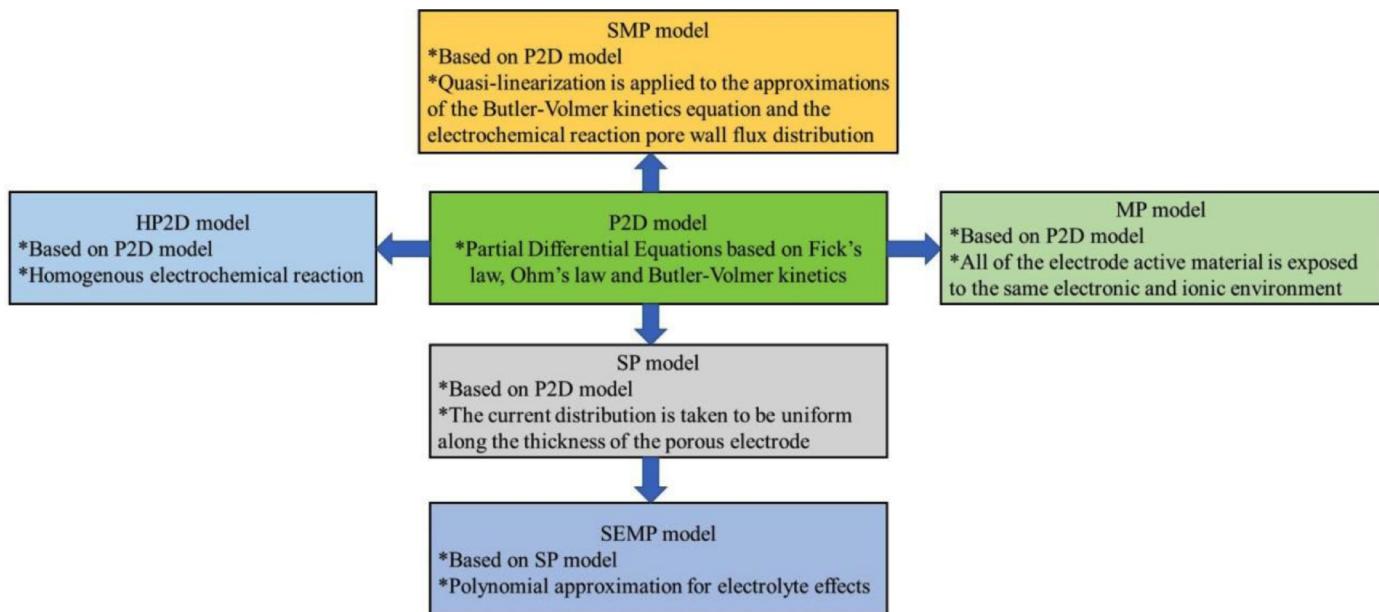


Fig. 1. Some relevant model assumptions and simplified methods of P2D model

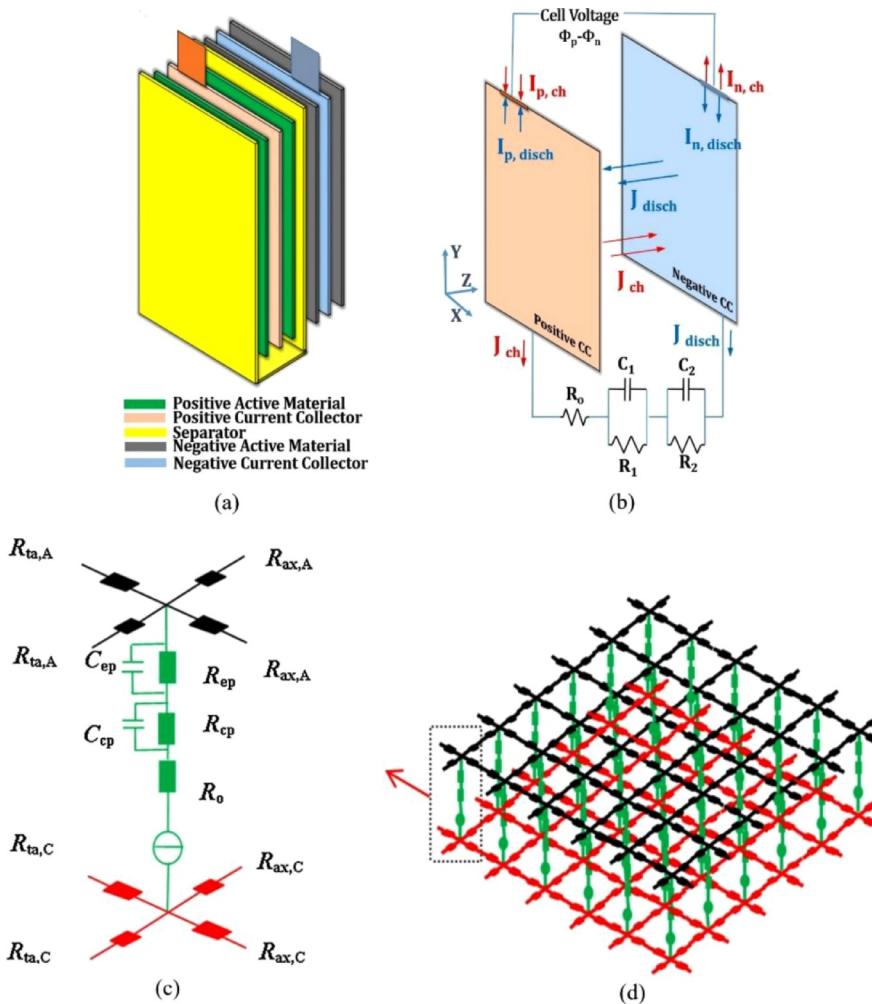


Fig. 2. (a) Schematic of battery cell internal architecture, (b) Schematic of 2d potential distribution model on a pair of parallel positive and negative current collectors [56]; Illustration of the cell element equivalent circuit (c) and 2D network equivalent circuit. Polarization capacitances are not illustrated for better visualization (d) [59]

	Max	Deviation of Max.		Min	Deviation of Min.		Non Uniformity	Simulation Time / min
		Temp / °C	Temp M xTD / %		Temp / °C	Temp M nTD / %		
<i>Equation</i>		<i>MxT</i>	$\frac{MxT_{ms} - MxT_{mod}}{MxT_{ms}} \times 100$	<i>MnT</i>	$\frac{MnT_{ms} - MnT_{mod}}{MnT_{ms}} \times 100$	$\frac{MxT - MnT}{MxT} \times 100$		
Measured (ms)	54.2			48.8			10	
Models (mod)	FULL	54	0.5	49.5	-1.5	8.2	13	
	P2SIm 1	53.7	0.9	50.1	-2.7	6.7	7	
	P2SIm 2	53.1	2.1	49.3	-1	7.1	6	
	Th2SIm	51.5	4.9	48.5	0.6	5.9	1	
	UHM	52	4.1	49.4	-1.3	4.9	4	

Fig. 3. Comparison of accuracy and simulation time of different models [56]

dependence of electrical parameters and temperature on polarization resistance and Ohmic resistance as well as dependence of electrical parameters on reversible thermal term is established by some data fitting methods. And the heat generation term obtained according to the above dependent relation which is substituted into the thermal model to solve the battery temperature distribution. Xie et al [61] innovatively used neural network model to draw the dependence of ohmic resistance, polarization resistance on SOC, temperature and current rate. Comparing with the experimental data, the neural network model predicted the temperature distribution of the battery well. This method can avoid the establishment of some electrical models based on complex higher order partial differential equations and greatly reduce the calculation time and improve the calculation efficiency. Based on some other fitting methods, we can refer to the researches of Yang and Lei et al [62,63].

2.2.3. Thermal runaway model

For the thermal runaway model, the early more mature mathematical model was developed in the research of Kim et al [81] which introduced Arrhenius equation to calculate reaction rate so that obtaining the heat generation of chemical degradation reactions. The total heat generation of the battery when the thermal runaway happens is expressed as:

$$Q_{total} = Q_{sei} + Q_{ne} + Q_{pe} + Q_{ele} + Q_{nb} \quad (2)$$

where Q_{sei} is the heat from the SEI (solid electrolyte interphase decomposition reaction), Q_{ne} the reaction between the negative active material and electrolyte, Q_{pe} is the reaction between the positive active material and electrolyte, Q_{ele} is the electrolyte decomposition, and Q_{nb} is the reaction between the negative active and binder.

Zhao et al [82] developed a thermal model to analyze the temperature distribution and heat characteristics of separator under the condition of thermal runaway of a lithium-ion battery cell. The experiment in this paper by local heating cathode current collector surface under different heat dissipation conditions showed that when the heat dissipation coefficient of the battery reached $10 \text{ W}/(\text{m}^2 \cdot \text{K})$, it could effectively control the occurrence of battery thermal runaway, but the temperature distribution uniformity of the separator surface became worse. It can be seen from the experimental results that the trend of temperature change in experiment and simulation is basically the same and the maximum temperature difference between experiment and simulation is less than 10 K. Furthermore, the error is less than 2.5% which shows the experimental results are in good agreement with the simulation results [82]. Generally speaking, over-charge (or over-discharge) is easy to cause the battery thermal runaway. Therefore, the heat generation of chemical degradation reactions of batteries under over-charge (or over-discharge) conditions established by some researchers [60,83–85] was also calculated based on Eq. (2). Fig. 4 depicts an overview of the overcharge side reactions at each stage for

lithium ion batteries with NCM+LMO cathode, in which NCM and LMO denote LiNiCoMnO_2 and LiMn_2O_4 , respectively. Sara Abada et al [85] developed a thermal runaway model which takes the effects of battery calendar aging factors into account and combines a zero-dimensional (0D) calendar ageing model with the model of Kim et al. [81].

The combination of simulation and experiment proved that the battery calendar ageing led to a delayed onset of the cell self-heating temperature with a thermal runaway starting at a lower temperature [85]. In terms of the aging factors, the continuous formation of the SEI (solid electrolyte interface) layer over the surface of the negative electrode considered as the most likely ageing mechanism, have been described by many physics-based models [85–88]. However, some researchers suggested that the loss of cathode active material also played an important role during the degradation of the cells [89,90]. In the research of Yang et al [89], the growth of SEI film and the loss of electrode active materials were considered as calendar aging factors. Then, an improved mathematical thermal model which took the SEI film growth and the lithium plating as the main side reactions was developed based on Tafel equation and P2D model. Simulation results indicated that the aging of the battery was dominated by various aging factors under different operating conditions. Higher ambient temperature could accelerate SEI formation reaction, while low temperature could cause severe lithium-plating. Active material loss was affected by cycling current significantly so that it became the dominant aging factor under extremely high current-rate. It can be concluded that high current-rate, high temperature and low temperature can lead to the acceleration of capacity loss of the battery and then accelerate battery aging process, but the dominant aging factors are different under above different conditions [89]. In general, above models are proposed to predict battery aging behavior also known as the calendar aging models. However, the main safety issue with aging batteries is thermal runaway so that the calendar aging model can be regarded as a special thermal runaway model.

2.3. Summary

In this section, some battery thermophysical models are reviewed in detail. For the simulation calculation time and calculation accuracy of various models, the following tables can be obtained: Table 1 (reduced order simplified model), Table 2 (physical structure simplified model) and Table 3 (electro-thermal model). For the reduced order simplified model, the calculation time of Laplace transformation and polynomial approximation is reduced to a certain extent compared with the original model, but the calculation accuracy is lower than other models. The calculation time of Galerkin's method can reach 0.094s, and its calculation accuracy is relatively higher, so it is an ideal method for simplification of order reduction. The number of equations solved by HP2D and SEMP models is much less than that of the original P2D model, and

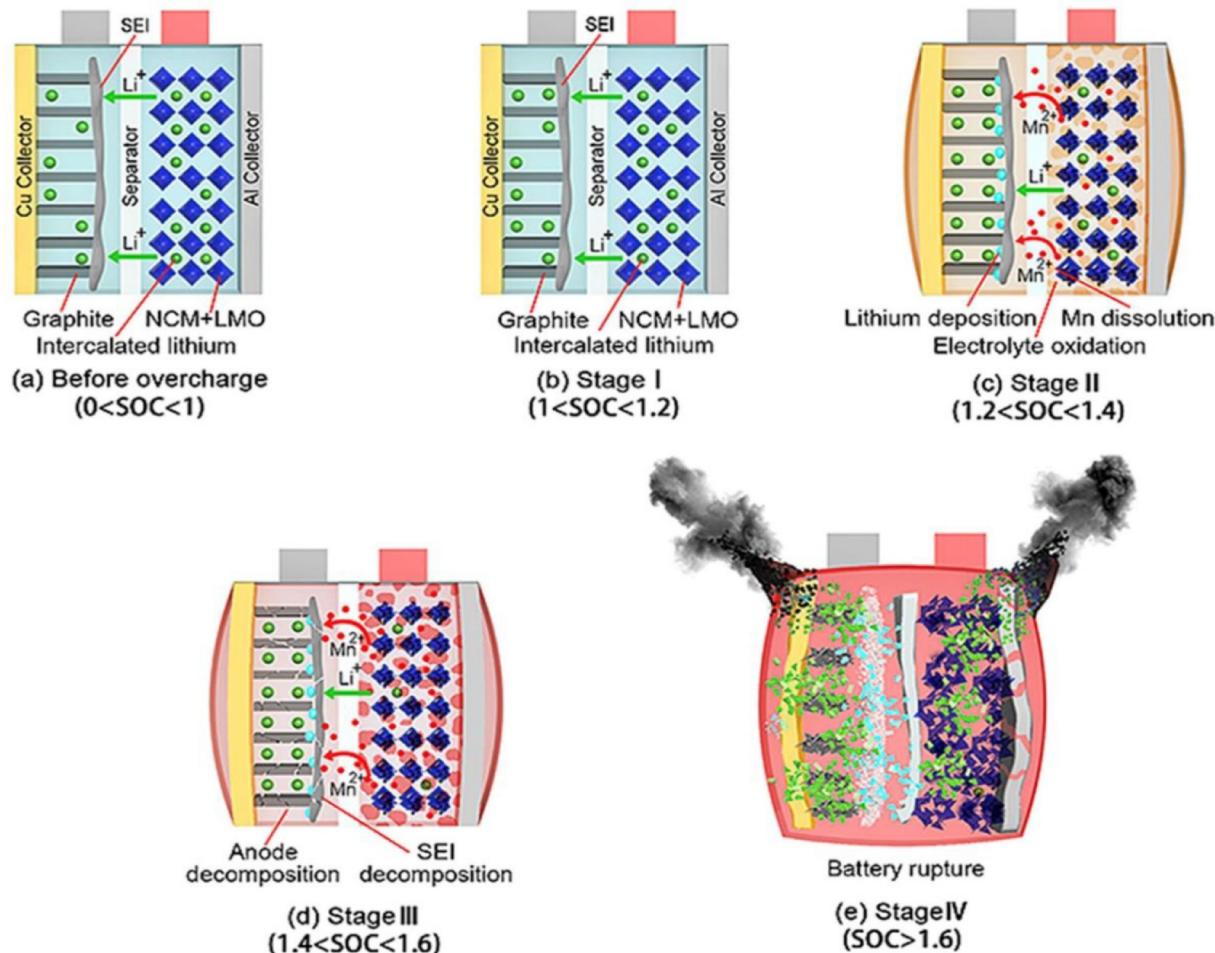


Fig. 4. Overview of the overcharge side reactions at each stage for lithium ion batteries with NCM + LMO cathode [83]

their calculation accuracy is close to each other. When N is small, the number of equations to be solved by SEMP model is close to that of HP2D model. However, when N is large, SEMP model needs to solve more equations than HP2D model so that HP2D model is more suitable than SEMP model. Compared with the original P2D model, the calculation time of SMP, SP, MP and ESP is shortened by nearly two orders of magnitude. At 5C discharge, the calculation time of SMP model needs 0.3402s, which is longer than that of other models. However, the calculation accuracy of SMP model is the highest and the calculation time is acceptable. Therefore, SMP model is more suitable for occasions with higher calculation accuracy. In addition, it can be seen from Table 3 that the calculation accuracy of the electro-thermal model based on the equivalent circuit method (as shown in Fig. 2 (c) and (d)) is higher than that of some parameter fitting models. Moreover, the more RC elements are set in the equivalent circuit, the calculation accuracy will be improved but the calculation time will be correspondingly longer [57]. Some fitting methods are used to find out the dependence of electrical parameters and temperature on polarization resistance and Ohmic resistance, then solve the total generated heat produced by combining ohm's law. Since the above type of fitting method requires the measurement of some electrical parameters, such as SOC (State Of Charge). The accuracy of the model requires the accuracy of the measured data. SOC is not always sufficiently precise to measure in dynamic cases such as current in electric vehicles. Through the Kalman filter [61], we can obtain the change of SOC in dynamic cases to solve above problems. For the battery thermal runaway model, the further improvement of chemical degradation reactions is an effective method to improve the accuracy of battery thermal runaway model. However, the calculation

cost will also increase correspondingly.

Where m_0 is the parameter calculated by the P2D model, which is established by the battery used in the corresponding paper; m_{smp} is the parameter calculated by the simplified model, and m_{exp} is the parameter measured in the experiment.

3. Battery cooling technology based on solid-liquid phase change materials

3.1. Introduction of phase change materials and their thermal properties

Phase change material could absorb or release a lot of heat called latent heat during the phase change process at a specific temperature [97,98]. On the other hand, according to the thermodynamics theory, the temperature of a substance remains basically the same when the phase change occurs so that phase change materials can be regarded as energy storage materials. Combined with above advantages, they can be used to adjust the temperature of working environment by phase change process to achieve the temperature control. The temperature control technology based on the characteristics of phase change materials has been used in many fields, such as solar energy utilization [99,100], waste heat recovery [101], building energy efficiency [102], battery heat dissipation [103] and other fields.

According to the theory of transformation thermodynamics, the phase change process refers to the process in which a substance changes from one phase to another. Furthermore, according to the thermodynamic classification, the common types of phase transition are first-order transition and second-order transition. The first-order transition

Table 1
The simulation calculation time and calculation accuracy of various reduced order simplified models.

Laplace transformation [69]	the orthogonal decomposition [70]	Polynomial approximation [72]	Galerkin's method [73]	the Padé approximation [74]	Dimensionless method [91]
The shortest solution time (s) Error range $ \frac{m_0 - m_{amp}}{m_0} \times 100\%$	Shorter than original model 0.13%–24.85%	1/7 solving time of the original model 0-0.3%	Shorter than original model 0-5%	0.094s 0-1.02%	290.35s (Shorter than original model) 0.01%-0.25%

refers to the unequal first order partial derivative of the chemical potential to the pressure or temperature when the phase change occurs and the two phases are in equilibrium. The relevant mathematical relationships can be expressed by Eqs. (3)–(6).

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (3)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (4)$$

$$S_1 \neq S_2 \quad (5)$$

$$V_1 \neq V_2 \quad (6)$$

where G is the Gibbs free energy, P is the pressure, T is the temperature, S_1 and S_2 are the entropy before and after the transformation, V_1 and V_2 are the volume of the substance before and after the transformation. From the above relationship, it can be seen that the volume of the material changes with the occurrence of the first-order transition, and the heat absorption or exothermic phenomenon occurs. The common solid-liquid phase change, liquid-gas phase change and solid-gas phase change are all attributed to the first order transition. For example, when ice melts into water at the same temperature, it needs to absorb heat and its volume becomes smaller so that this phase change also belongs to the first order transition. For the second-order transition, the volume of the substance does not change and there is no heat absorption or exothermic, but the thermodynamic parameters such as the coefficient of thermal expansion and the specific heat capacity have changed, which satisfies the Ehrenfest equation. The transition between conductor and superconductor is a common second order transition.

3.2. Thermal management of phase change materials based on metal salts, hydrates and eutectic compounds

Inorganic phase change materials mainly include metal salts, hydrate salts and some eutectic compounds [104]. Most metal salts, such as nitrates, carbonates, and sulfates, have high melting points and are suitable for the medium and high temperature thermal storage applications at 200~1000°C [105,106]. Most of the hydrate salts have a solid-liquid phase change temperature below 60°C [104,107] which is much lower than metal salts. Theoretically, they can be used as phase change materials for battery thermal management. On the other hand, although there are some effective methods to promote the thermal conductivity of hydrate salt and improve the phase separation as well as supercooling phenomenon [108], there is no effective way to improve its melting heat. Furthermore, the properties of the eutectic hydrated salt are similar to those of hydrate salt.

In order to overcome the problem of low melting heat, Liu et al [109] added TiO₂ nanoparticles to Na₂CO₃•10H₂O-Na₂HPO₄•12H₂O. The enthalpy of phase transition and specific heat capacity were measured by Differential Scanning Calorimeter (DSC). Results showed that both were significantly improved. This method can be used in the thermal management of lithium-ion batteries in the future. In addition to hydrate salts, hydrates also contain organic hydrates. Ryo Koyama et al [110] measured and studied the thermal performance parameters of trimethylolethane (TME) hydrate. It was found that when the mass fraction of TME in the prepared TME aqueous solution was 0.6, the TME hydrate obtained by cooling crystallization had ideal dissociation heat and the value was 190.1kJ/kg as well as the phase transition temperature was 29.6°C. Therefore, the above characteristics can be used as phase change material (PCM) for cooling lithium-ion batteries in electric vehicles. Generally speaking, hydrates are crystalline compounds consisting of water molecules, the host compound, and other compounds which are called the guest compound. The thermal properties of hydrates depend on the guest compounds [110]. At present, the application of hydrate phase change materials in the field of thermal

Table 2

The simulation calculation time and calculation accuracy of various physical structure simplified models.

	P2D [77,79]	HP2D [79]	SEMP [79]	SMP [77]	SP [76,77]	MP [77]	ESP (The extended single particle model) [77]
The shortest solution time (s) or the number of equations	The number of equations 51 + 210 × N (N is a positive integer) The shortest solution time 1C-discharge:141.654 3C-discharge:60.958 5C-discharge:43.711	The number of equations 51 + 21 × N	The number of equations 12 + 42 × N	solution time 1C- discharge: 1.8334 3C- discharge: 0.5844 5C- discharge: 0.3402	solution time 1C- discharge: 0.0189 3C- discharge: 0.0066 5C- discharge: 0.0045	solution time 1C- discharge: 1.097 3C- discharge: 0.3017 5C- discharge: 0.1714	solution time 1C- discharge: 0.1645 3C- discharge: 0.0418 5C- discharge: 0.0249
Error range $ \frac{m_0 - m_{smp}}{m_0} \times 100\%$	—	0-1.5%	0-2.5%	0-0.3%	1.5%-3%	0-1.5%	0-4.2%

management of lithium-ion batteries is relatively few. According to the above existing research results, in the future, the corresponding hydrate can be synthesized by using the guest complex with appropriate thermal physical properties as PCM for thermal management of lithium-ion batteries.

3.3. Thermal management based on enhanced organic phase change materials

Organic phase change materials, such as the most commonly used paraffin, have the advantages of high latent heat, no toxic, no corrosive, stable chemical properties and no supercooling. However, their disadvantages mainly lie in low thermal conductivity [13,111] so that the absorbed heat cannot be quickly discharged to the outside environment. In order to improve the thermal conductivity of pure paraffin, researchers add nano materials [112,113], porous materials [114,115], metallic materials [41,116] and other carbon based materials to enhance the heat transfer of paraffin. In addition, the volume of paraffin changes after the phase transition occurs as well as the shape may change after several solid-liquid phase transition cycles which could affect its thermomechanical properties. Furthermore, the molten liquid paraffin is easy to leak in the equipment. In view of the above problems and solutions, the article also gives an overview in this section.

3.3.1. Enhanced organic phase change materials based on nano materials

At present, nano materials used to enhance pure phase change materials include nano carbon materials, nano oxide materials and metal nano materials. Among them, carbon nano materials mainly include carbon nanotubes [112,117], carbon nanofibers [113], graphite nano powder and graphene nano sheet [118]. Wang et al [112] added carbon nanotubes into hexadecylic acid to prepare the cetyllic acid /carbon nanotubes composite phase change material. After adding carbon nanotubes, the thermal conductivity of the composite phase change material was significantly higher than that of the pure hexadecylic acid material. In addition, whether in the solid or in the liquid state, the thermal conductivity of the composite increased with the increase of the mass fraction of carbon nanotubes. In the study of Zou et al [117], Multi-walled carbon nano-tubes (MWCNT) based, graphene based and MWCNT / graphene based composite phase change materials were prepared and experimentally investigated. For MWCNT / graphene based composite phase change materials, the results denoted that

they could show the best synergistic heat transfer enhancement effect when their mass ratio was 3/7 and its thermal conductivity had been significantly improved. In addition, it could also inhibit the rapid temperature rise of liquid PCM, which showed the great potential of thermal management of power Li-ion batteries. Nano oxides include nano metal oxides [119] and nano non-metallic oxide [120].

Bondareva et al [119] added nano alumina into paraffin and investigated the heat and mass transfer in the enhanced phase change material by establishing a mathematical model of fin radiator with paraffin as phase change material. The results of computer simulation showed that the melting process of paraffin in the initial stage was accelerated after adding nano alumina. However, the viscosity of liquid paraffin increases with the volume fraction of nanoparticles, which could weaken the flow capacity of liquid paraffin and affect the thermal convection between PCM and the external environment. In order to alleviate the leakage of PCM in the melting process, the volume change and inhomogeneity of the whole module during the repeated melting / solidifying processes, Lv et al [120] developed a nano-SiO₂ enhanced composite PCM (CPCM-NS) which had excellent anti leakage and anti volume change properties for thermal management of power batteries. Nano silica has a considerable amount of nano sized pores, which can effectively inhibit the migration and leakage of the melted paraffin through the adsorption of these pores. The experimental results showed that the enhanced performance of CPCM-NS yielded better cooling efficiency and durability of the obtained battery module.

For metal nanomaterials, most of them are applied to improve the thermal conductivity of pure phase change materials [121]. Karimi et al [122] added copper, silver and Fe₃O₄ nanoparticles into paraffin to improve the heat transfer rate. According to the experimental results, all the nanocomposites of PCM increased the heat transfer potential of the system, but the composites containing Ag nanoparticles showed better thermal performance than other composites.

With the addition of more nano materials, the thermal conductivity and stability of materials could be better. However, the amount of pure phase change materials per unit volume of composite materials will be less, which inevitably leads to the decrease of latent heat of composite phase change materials. Furthermore, Bondareva et al. [119] also showed that the flow capacity of liquid paraffin decreased with the added nano alumina. On the other hand, the density of nano metal or its corresponding oxides is larger than that of pure phase change materials. When PCM melts, the particles of the additives would settle under the

Table 3

The simulation calculation time and calculation accuracy of Electro-thermal models.

	Equivalent circuit model [56]	Equivalent circuit model [57]	Parameter fitting model [61]
Solution time of simplified model (s)	60-780	—	—
Error range $ \frac{m_{exp} - m_{smp}}{m_{exp}} \times 100\%$	Error range of temperature 0.5%-4.9%	Error range of temperature 0-5.6% Error range of voltage 0-0.74%	Error range of temperature 0-33.9%

Table 4
Properties of some enhanced phase change materials.

Reference	CPCM	Mass ratio of additive(wt %) or volume ration of additive(v%)	Latentheat(kJ/kg)	Meltingpoint(°C)	Soliddensity(kg/m ³)	SpecificHeat(kJ/kg·K)	Thermalconductivity(W/m·K)	Max thermalconductivityenhancement($\frac{k_c - k_0}{k_0}$)%
[112]	Palmitic acid/treated MWCNT	0.2-1wt%	184-208	61.1-62.4	-	-	0.24-0.4	46%
[117]	Paraffin (PA)/graphene/MWCNT	1wt%	198.0-203.8	40.8-45.3	-	-	0.61-0.82	124%
[119]	n-octadecane/nano-Al ₂ O ₃	0.8vol%	-	-	-	-	0.15-0.5	33.8%
[120]	PA/ Expanded Graphite (EG)/Low-density polyethylene (LDPE)/Nano-SiO ₂	37-44wt%	70.4-81.7	44	-	-	1.15-3.26	200%
[122]	PA/Ag-nanoparticles; PA/Cu-nanoparticles; PA/Fe ₃ O ₄ -nanoparticles; PA/metal matrix	2wt%	-	-	-	-	-	250%
[9]	PA/EG/copper mesh	-	141.6	40-50	-	-	7.65	2842%
[123]	PA/EG/LDPE/Aluminum Fins	-	87.4	44.5-50.2	856	2.48	1.38	763%
[126]	PA/copper foam	-	-	25-48	-	3.35-10.55	2.88-3.11	4638%
[40]	PA/aluminum foam	10-30vol%	-	46-52	-	-	46.04-46.12	2132.4%
[148]	PA wax (PW)nick foam	-	120	37	-	1.7	1.2	33.3%
[148]	PW/graphene coated nick foam	-	99	38	-	1.6	4.6	411%
[139]	PCM/EG	15-25wt%	50.3-73.4	44-52	700-1040	2.5-2.9	5.3-11.2	-
[147]	PCM/graphene	-	160	32-38	895	1.91	6-25	-
[98]	PA/Epoxy Resin (ER) / SiC	15-20wt%	100	-	-	-	2.0-2.8	1072%
[111]	PA/EG/ER/Aluminum nitride	0-25wt%	114.5-178.4	-	-	-	1.5-4.3	2050%

action of gravity. After several solid-liquid phase change cycles of PCM, most of the nano materials are located at the bottom of pure PCM so that making their distribution in PCM uneven and greatly affects the heat transfer enhancement effect of nano materials on pure phase change materials.

3.3.2. Enhanced organic phase change materials based on metal materials

Most metal materials have excellent thermal conductivity, and many researchers embedded them into pure PCM to make up for the defect of low thermal conductivity of pure PCM. Metal materials commonly used to enhance the thermal conductivity of pure phase change materials include metal mesh [9,41], metal fins [116,123], metal fiber [124] and metal compounds [111]. The metal mesh is usually placed between different PCM units in a sandwich structure. As shown in the Fig. 5(c) and (d), it is not covered by PCM at the edge and contacted with the external environment.

The natural convection of the surrounding air could be improved with the increase of metal mesh temperature, which results in the heat dissipation effect more ideal. In the study of Wu et al [9], a new composite phase change material was prepared by embedding copper mesh into the phase change material composed of paraffin and expanded graphite. Expanded Graphite (EG) with porous structure can absorb liquid Paraffin (PA) and prevent PA leakage. The thermal conductivity and mechanical strength of the whole module can be further improved by embedding Copper Mesh (CM) into two PA / EG materials to act as composite PCM framework. The experimental results showed that compared with the Phase Change Material Plate (PCMP) without CM, the CM enhanced PCM with PCMP had better heat dissipation performance and temperature uniformity, especially in poor working conditions. Sadrameli et al [125] filled polyethylene glycol which was used as a phase change material between aluminum mesh plates to manage heat dissipation of the whole battery pack and a simulation mathematical model was established by computer. The experimental results denoted that the surface temperature could be significantly reduced by using PCM and aluminum mesh between batteries, and the battery pack showed better performance. For the charge discharge rates of 1C, 2C and 3C, the maximum cell surface temperature at ambient temperature decreased by 19%, 21% and 26%, respectively. In addition, the results of the mathematical model agreed well with the experimental data and the deviation was acceptable, which showed that the model had certain accuracy.

For the organic phase change materials enhanced by metal fins, there are two ways to combine them with phase change materials: one is to embed the fins in PCM, the other is to place the fins on the outer surface of PCM [126]. As shown in the Fig. 5(a), (b) and (c) above. The submerged fin structure can reduce thermal resistance, and the low thermal resistance is beneficial to enhance the cooling effect of the system [125]. Wang et al [116] tested the thermal behavior of cylindrical battery by the composited paraffin and fin structure. They placed vertical straight fins on the cell side of the cylindrical model and immersed them in paraffin, then the thermal enhancement with the PCM-fin cases was examined experimentally. Following the experimental results, the logarithmic dependence of the time-averaged Nusselt number was correlated with the heat transfer area ratio and the composite PCM fin system had the advantages of good thermal performance as well as long working time. Lv et al [123] built a novel thermal management system by setting aluminum fins on the outer surface of the composite phase change material composed of expanded graphite, paraffin and low-density polyethylene and then embedded the batteries into the composite phase change material. The skeleton composed of Low-Density Polyethylene (LDPE) and expanded graphite can not only enhance the mechanical properties of paraffin, but also prevent paraffin leakage to a large extent. The lower fins placed on the outer surface of phase change material make the Battery Thermal Management System (BTMS) have higher surface heat transfer capability. The experiment also proved that LDPE / EG / PA composite PCM had better mechanical

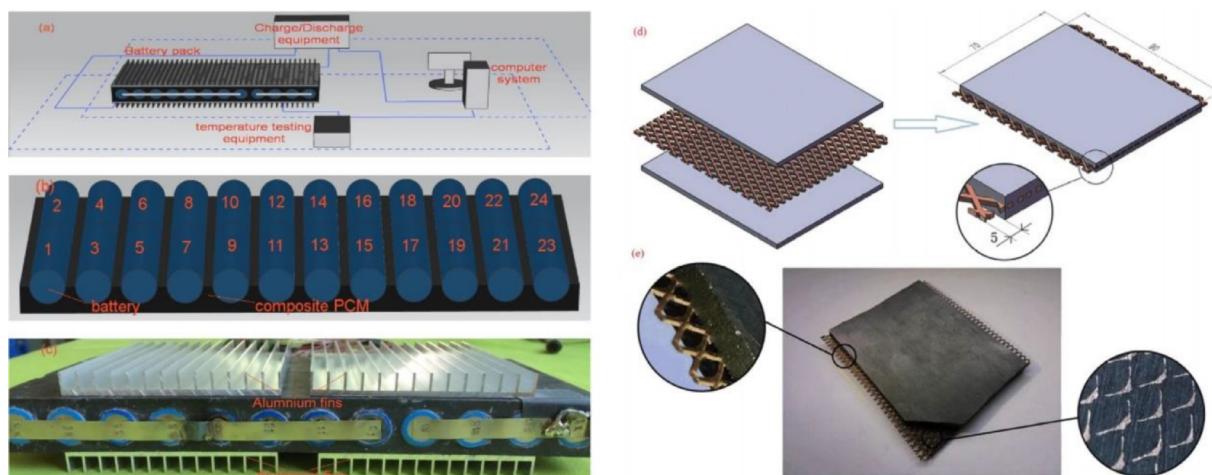


Fig. 5. (a) Schematic diagram of the experimental system (b) Diagrammatic cross-section of the battery pack with L-CPCM (c) Battery pack coupling L-CPCM with heat dissipation fins [123] (d) Fabrication of scheme (e) and photograph of CM based CPCM (d) [9]

properties and cooling effects than EG / PA composite and air cooling respectively.

Weng et al [127] set the same number of triangular fin, rectangular fin and circular fin on different cylindrical battery side surfaces. Furthermore, a combined structure of 4 rectangular fins and 2 circular fins is also set. Through the experiment and analysis to the shape and number of fins, for the fin shape, the longitudinal and circular fins have respective strengths, longitudinal fins have a beneficial effect on heat dissipation by air convection, while circular fins show stronger heat conduction ability inside the PCM owing to their larger heat transfer area. For the number of fins, the most appropriate number of fins should be determined in combination with the space size of BTMS. However, for the above combined structure, the maximum temperature of the fin module was 29.1°C at 1C charging rate, which was 5.5% lower than that of the rectangular fin module. For the metal fiber, their application in battery thermal management is relatively few. Pan et al [124] prepared the corresponding composite phase change materials by embedding the cut copper fiber sintering skeleton into paraffin, and compared the new materials with the experimental data of pure paraffin and paraffin / foam copper composite phase change materials. Cut Copper Fiber Sintering Skeleton (CCFSS) / paraffin composite PCM effectively improved the heat transfer performance, and the temperature difference of the battery was kept within 5°C.

3.3.3. Enhanced organic phase change materials based on porous materials

Porous materials are commonly used in battery thermal management to enhance organic phase change materials include metal foam [114,128] and expanded graphite [115,129,130]. Metal foam has the advantages of small specific gravity, large specific surface area, high porosity, and high thermal conductivity. In addition, currently used foam metal includes copper foam [114,131], aluminum foam [40,132] and nickel foam [133]. The detailed structure is shown in the Fig. 6.

There are two ways to couple metal foam based composite phase change materials with batteries. The composite phase change materials combined in this way that embedding batteries or battery packs into composite phase change materials can improve the temperature uniformity of the battery surface or the temperature uniformity of the battery pack and enhance the heat transfer performance of the pure phase change materials. Rao et al [135] designed and used paraffin/copper foam composite phase change materials to conduct thermal management of the battery, and discussed the temperature change as well as temperature distribution of the system in detail. From the discharge experiments of single cell and battery module, the local temperature difference increased with the increase of discharge current. However, after adding copper foam / paraffin composite phase change

material, the maximum temperature and local temperature difference of the battery module under driving conditions were lower than 40°C and 3°C, respectively, and showed good cooling performance. Zhang et al [136] designed an optimized passive thermal management system by embedding copper foam/paraffin composite phase change material into the LiFePO₄ battery pack, and compared the two heat dissipation modes of air cooling and pure PCM. The experimental results showed that, as shown in the following Fig. 7, the copper foam / paraffin composites can significantly reduce the surface temperature of the battery due to the high thermal conductivity of copper foam compared with the other two heat dissipation methods at different discharge rates.

In addition, the foam copper / paraffin composite can make the battery pack have better temperature uniformity at higher discharge rate. In the study of Alipanah et al [137], a mathematical model of phase change heat transfer based on aluminum foam / octadecane composite phase change material was established to explore its cooling performance for batteries. Compared with different phase change materials, the temperature on the surface of the battery decreased more significantly based on the composite phase change material. Furthermore, the maximum temperature difference on the surface of the battery decreased from 25°C to 2°C compared with pure octadecane as phase change material which provides a theoretical basis for the application of aluminum foam / octadecane composite phase change materials in practical battery thermal management. On the other hand, they also found that the temperature uniformity of the battery surface is closely related to the convective heat transfer. When the convective heat transfer played a major role in the heat transfer, the temperature uniformity of the battery surface will decrease. Due to the addition of aluminum foam to the composite phase change materials, this greatly improved the thermal conductivity of octadecane so that the heat conduction and heat diffusion played a leading role in heat transfer.

Furthermore, the porous material can inhibit the flow of melted octadecane to a certain extent, and there will be a more uniform temperature distribution on the surface of the battery. Li et al [138] numerically investigated the effects of porosity and pore size on copper foam. Although the contact area between the foam copper matrix with lower pore density and the pure phase change material were smaller, which reduced the melting or curing rate, it was more favorable for natural convection. Qu et al [39] also did some similar studies. In addition, metal foam can also accelerate the melting process of phase change materials as well as porosity and pore density also have an important influence on the heat transfer ability of metal foam and the natural convection of liquid PCM. For detailed introduction, please refer to [31]. However, the batteries or battery packs can also dissipate heat without embedding into the composite phase change material.

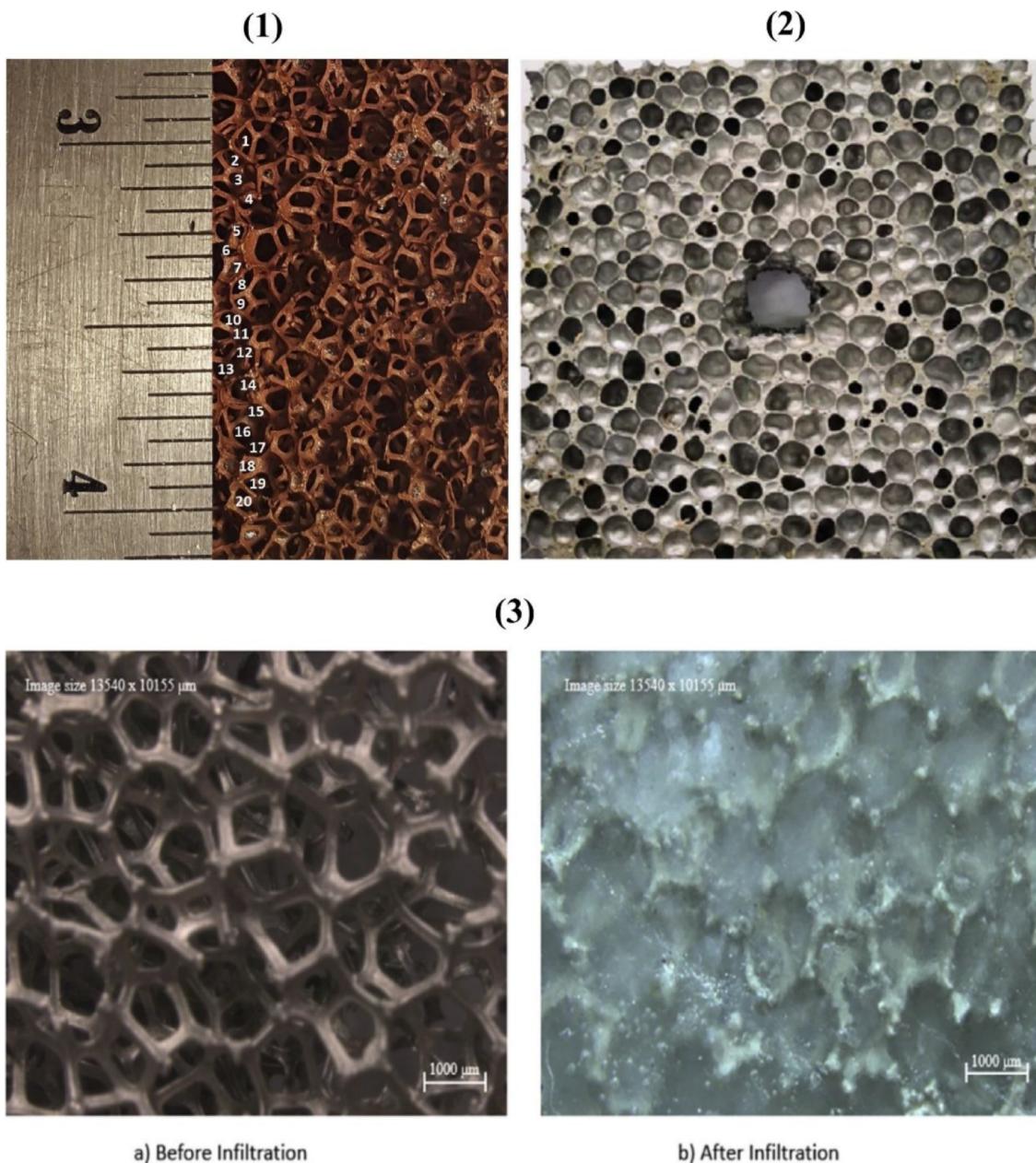


Fig. 6. Different structures of metal foam (1) Structure of copper foam [114] (2) Structure of aluminum foam [134] (3) Structure of nickel foam before and after infiltration of pure PCM [133]

Wang et al [33] designed a novel passive Thermal Management System (TMS) based on copper foam and paraffin composite phase change material (PCM) for lithium ion battery packs. As shown in the Fig. 8, there is indirect contact between Phase Change Storage Energy Unit (PCSEU) and batteries. Compared with pure Air Cooling System (ACS), pure ACS with air flow $\leq 200\text{m}^3/\text{h}$ cannot meet the requirements of battery temperature control. The experimental results showed that pure ACS could not only consume more battery power, but also led to higher temperature difference within the battery pack.

The new TMS could make the battery pack complete three 4C charge and discharge cycles at an ambient temperature of 35°C, while the maximum temperature was kept below 52°C.

For porous carbon materials, the representative is expanded graphite (EG). EG is embedded into the pure phase change material to form the composite phase change material. As a framework, the thermal mechanical properties and thermal conductivity of the pure phase change material can be improved. After several solid-liquid phase

change cycles, the shape of the composite phase change material can maintain stability as well as the leakage degree of the pure phase change material after liquefaction can also be significantly reduced. Ling et al [139] evaluated the performance of passive battery thermal management systems using paraffin/EG composites. According to the experimental results, the paraffin / EG composite material with density of 890kg/m^3 and paraffin content of 75% was proposed to be used in thermal management of power battery. The numerical simulation results were in good agreement with the experimental data. Lin et al [49] designed a composite phase change material thermal management system based on EG / paraffin based on square lithium ion battery cooling. The experimental results of constant current discharge showed that the temperature of the cell module with EG / paraffin composite phase change material was reduced by 32% and 37% respectively at I (current) = 40A and I = 80A when TMS was used. At higher discharge rate, the cooling effect of PCM was more obvious. However, with the increase of discharge time and current rate, the temperature uniformity

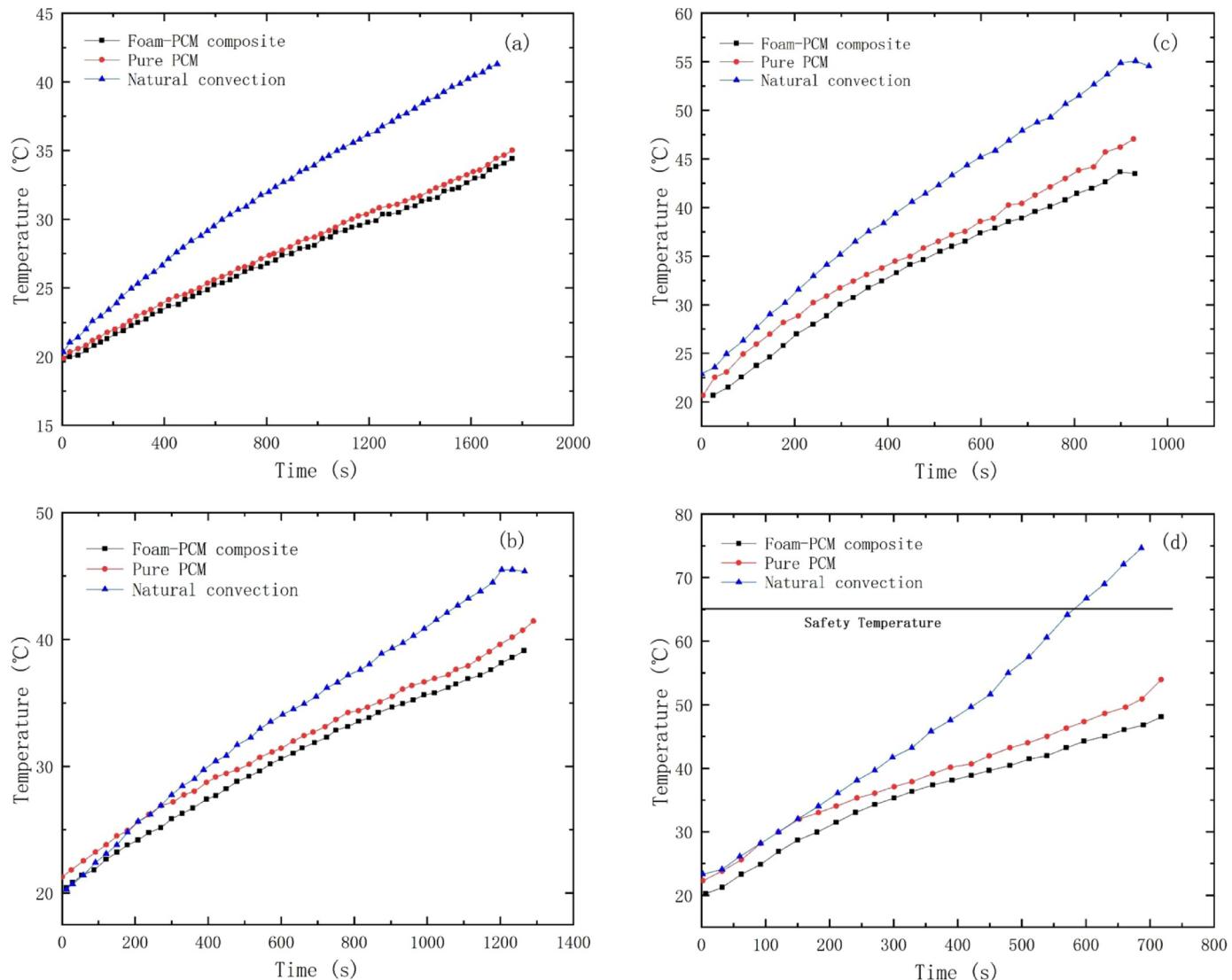


Fig. 7 Temperature variations with time under three dissipations: (a) 2C discharge rate, (b) 3C discharge rate, (c) 4C discharge rate, (d) 5C discharge rate [136]

on the module became worse. Although EG can improve the thermal conductivity of pure phase change materials to a certain extent, it cannot meet the thermal management of batteries under high rate and long-term discharge so that it is necessary to further improve the thermal conductivity of composite phase change materials.

In order to improve the thermal conductivity and secondary heat dissipation capacity of phase change material (PCM) in the application of thermal management (BTM), He et al [97] obtained a new type of composite phase change material (PCM) by adding copper foam into EG / paraffin / Epoxy Resin (ER). EG with porous structure can adsorb paraffin and act as a micro heat conduction framework to transfer heat to the adjacent CF framework. Then CF acted as a macro framework to transfer heat to the whole composite phase change material plate and enhance the heat transfer coefficient of the interface between the plate and air. The experimental results also showed that batteries coupled with Composite Phase Change Material (CPCM) included EG / CF (CPCM-EG / CF) had better cooling and temperature uniformity performance than those without EG / CF or CF, especially in the forced convection secondary cooling system. Furthermore, the battery pack with CPCM-EG showed stable and lowest maximum temperature as well as minimum temperature difference under forced air flow, which were 48.0°C and 3.9°C respectively. Cao et al [140] filled the EG/ Paraffin Wax (PW) / silica composite phase change material into honeycomb

aluminum for thermal management of the battery pack. After the compression test, the composite material showed excellent mechanical properties without cracking or deformation on the surface. And due to the existence of honeycomb aluminum, it also had a high heat dissipation efficiency. At 5C discharge rate, the maximum surface temperature of the battery with PW / EG / SiO₂ / honeycomb aluminum-CPCM was recorded as 45.1°C, which was just within the allowable working temperature range of a typical LiFeO₄ battery system.

However, the composite phase change material based on EG with good thermal mechanical properties improves the strong rigidity and flexibility of the pure phase change material, which will inevitably lead to the installation difficulty of PCM, brittle damage and poor contact with the battery surface so that causing high contact thermal resistance on the contact surface. These problems can be solved by adding flexible polymer materials to the EG based composite phase change materials [141]. It should be also noted that the conventional strategy to improve the thermal conductivity of CPCM may cause another neglected safety problem: the conductivity of CPCM module is significantly improved due to the addition of carbon or metal components. In order to solve these problems, instead of metal materials, materials with high thermal conductivity and high resistivity can be used to combine with composite phase change materials based on EG, such as silicon carbide [98] and aluminum nitride [111]. The composite phase change material,

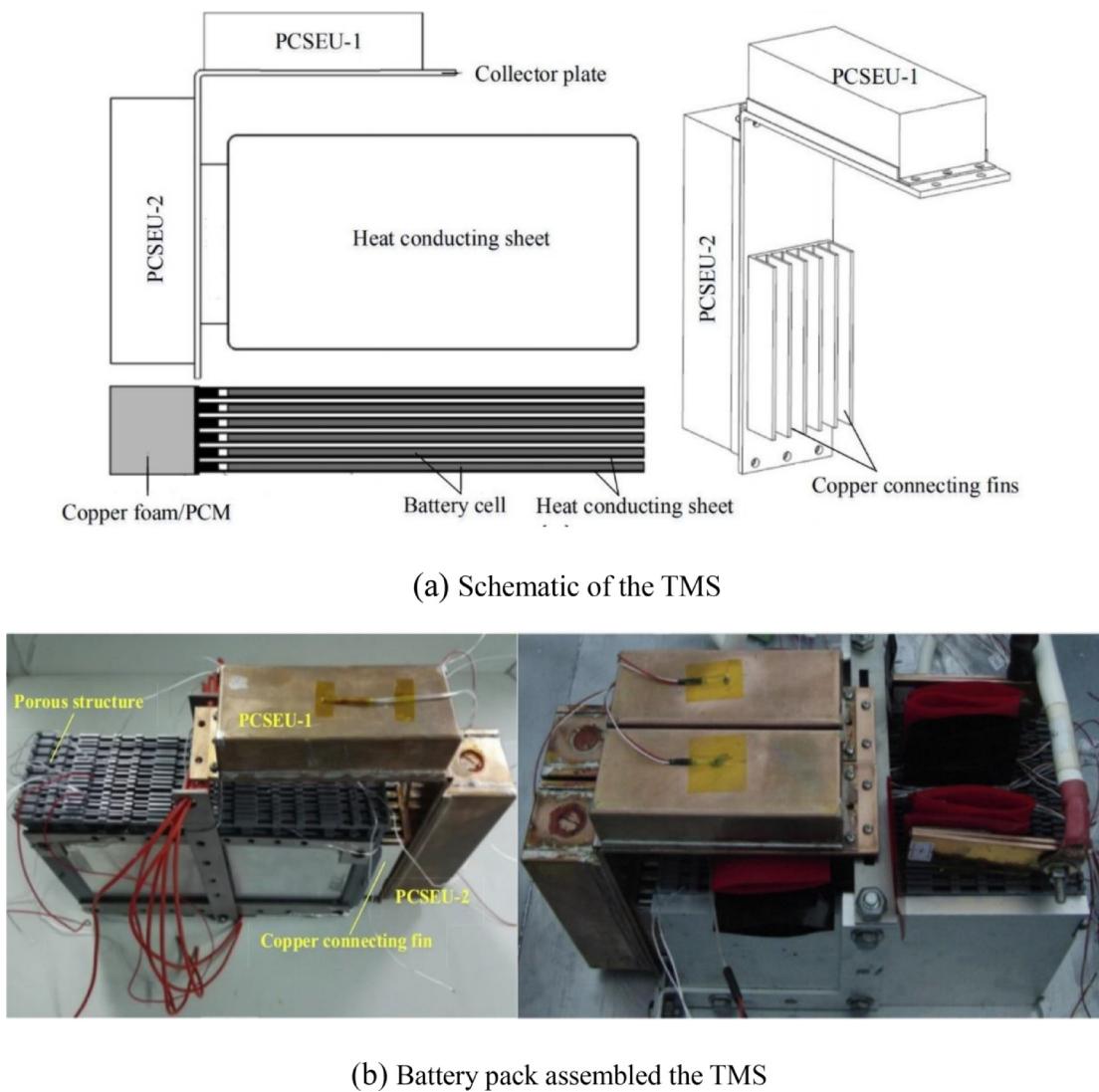


Fig. 8. TMS based on copper foam and paraffin composite phase change material [33]

which combines nontoxic porous concrete and EG / pure phase change material, can not only meet the requirements of thermal management of battery, but also reduce the use of graphite adsorbent. Moreover, the price of concrete is lower than that of graphite adsorbent, which is very consistent with the concept of sustainable and economic development [142].

3.3.4. Enhanced organic phase change materials based on other carbon materials

By adding other highly conductive carbon materials such as graphene [143,144] and carbon fiber [53,145] into pure phase change materials can also be used for effective thermal management of batteries. Graphene has high intrinsic thermal conductivity and good adhesion with a variety of matrix materials. In addition, the thermal conductivity of graphene enhanced composite PCM is two orders of magnitude higher than that of traditional PCM, while retaining its potential heat storage capacity [146]. Malik et al [147] used a rectangular Phase Change Composite material (PCC) based on PCM and graphene for thermal management of lithium ion battery packs. The experimental results showed that the maximum and average temperature of the battery pack were kept within the required limits ($25^{\circ}\text{C} - 40^{\circ}\text{C}$) at all selected discharge rates, but at high discharge rates, the melted PCM will leak from the PCC board. Furthermore, graphene can also be combined with other materials to further improve the thermal

conductivity of the original materials. Hussain et al [148] applied paraffin-saturated Graphene-coated Nickel (GcN) foam as a composite phase change material to the thermal management system of batteries. The thermal conductivity of graphene coated on nickel foam by chemical vapor deposition was increased by 23 times after liquid paraffin was infiltrated into GcN foam. The experimental results showed that the surface temperature of the cell decreased by 17% compared with the nickel foam after using the paraffin covered graphene coated nickel foam as the thermal management material under the discharge current of 1.7 A. In addition, compared with the latent heat of pure paraffin, the latent heat of paraffin covered nickel foam decreased by 30% due to the decrease of the mass fraction of pure paraffin in the inner part of the nickel foam coated with graphene. For graphene based composite phase change materials, it cannot absorb the melted pure phase change materials as expanded graphite can so that to inhibit its leakage. In another aspect, the thermal conductivity will be increased while the latent heat of composite phase change materials will be decreased for the method of combining graphene with other high thermal conductivity materials to further improve the thermal conductivity. Therefore, the balance between thermal conductivity and latent heat of phase transformation melting is needed to optimize the thermal management of batteries.

Compared with metal, carbon fiber is also a kind of carbon material with high thermal conductivity and this carbon based material has superior thermal performance, outstanding chemical stability, larger

specific surface area as well as lower density so that it is more suitable to be used as thermal conductive filler [53]. Some related studies can be referred to [53,145].

3.4. PCM capsule and its enhanced heat transfer

The solid-liquid phase change material has a significant heat dissipation effect in the thermal management of battery. However, the melting of solid phase change material will lead to the leakage of phase change material from the battery pack, which will affect the heat dissipation performance of PCM. In order to solve the problem of leakage, some porous materials such as expanded graphite that coupled with pure phase change materials were used to reduce the degree of leakage [115,129], but still cannot stop the leakage completely. In addition, the amount of pure phase change material per unit volume will be reduced after adding expanded graphite, which will lead to the decrease of latent heat of phase change material. Therefore, some researchers proposed to capsulize PCM [149]. Compared with the porous material embedded in the pure phase change material, the PCM is completely encapsulated by the capsule, which makes the solid-liquid phase change completely happen in the capsule so that the melted pure phase change material will not leak to the outside and greatly reducing the leakage degree of the melted PCM.

At present, the wall materials of PCM capsule are mostly organic polymer materials, including polymethylmethacrylate, High and low density Polyethylene (HDPE), biodegradable polymer, styrene maleic anhydrous copolymer and other inorganic materials combined with organic polymer materials [149,150]. However, most organic polymers have poor thermal conductivity [151,152] so that reducing the thermal conductivity of PCM inside the capsule. In order to improve the thermal conductivity of PCM capsule or its heat transfer fluid, the researchers put forward some optimization measures [153,154]. Park et al [153] added magnetic Fe_3O_4 nanoparticles to PCM nano-capsule and obtained PCM nano-capsule with weight percentages of 3.1%, 5.7% and 6.6%, respectively. The results showed that after the magnetic Fe_3O_4 was added, the supercooling degree of paraffin decreased and the thermal conductivity of nano-capsule was significant increased. In order to solve the problem of poor heat transfer performance of PCM microcapsules, Wang et al [154] added nano titanium dioxide to its suspension as heat transfer enhancement material, and the microstructure before and after adding nano titanium dioxide was shown in the Fig. 9. The results showed that the thermal conductivity of PCM microcapsules was obviously improved by adding a small amount of nano titanium dioxide into the thermal fluid with the content of 5%-20%. At present, PCM capsule technology has not been well applied to battery thermal management, which is mainly due to the high cost of its manufacturing.

3.5. Summary

In this chapter, some methods to overcome the low thermal conductivity of pure paraffin are summarized. The properties of some enhanced phase change materials are shown in Table 4. The first method is to find a substitute for paraffin, such as inorganic phase change material or hydrate phase change material, which has higher thermal conductivity than pure paraffin [108,110]. For some inorganic phase change materials or hydrate phase change materials with low melting heat, the corresponding methods are also proposed to improve the melting heat of materials. The second method is to improve the overall thermal conductivity of pure paraffin by adding high thermal conductivity materials, mainly including some nano materials, carbon materials and metal materials. Nevertheless, the addition of a single material can improve the thermal conductivity of paraffin, but it cannot take into account some other problems, such as the leakage of liquid paraffin, the shape stability of paraffin as well as the thermo-mechanical properties of paraffin. Therefore, it is the focus of future research to mix various additives with paraffin in a certain proportion to obtain the

corresponding composite phase change materials. The thermal management mode of indirect contact between the thermal management module based on composite phase change materials and the battery module also shows good performance. This indirect contact method can effectively avoid some problems caused by the direct contact between the phase change material and the battery module, such as the corrosion of the phase change material to the battery module and the short circuit of the battery module. In addition, in view of the leakage of liquid phase change materials, the phase change materials can be encapsulated. However, the thermal conductivity of most PCM capsules is poor, and some methods to improve the thermal conductivity are also introduced in this chapter.

4. Thermal management of batteries based on liquid-vapor phase transition principle

The battery thermal management technologies based on phase change materials introduced in the previous section belong to the temperature control of the battery through the solid-liquid phase change process of the materials. However, the liquid-gas phase transition principle can also be used for effective thermal management of the battery, which typically includes heat pipe cooling and boiling cooling. Most heat pipes are made of metal and have good heat transfer properties [155–157]. The commonly used heat pipe consists of three parts: the main structure is a closed hollow metal tube and the internal cavity contains the working medium as well as the inner wall of the metal tube has a wick structure (Some heat pipes do not have). It is well known that the lower air pressure in the environment, the lower boiling point of the liquid. In order to control the liquid-gas phase transition temperature within the temperature range which is suitable for the thermal management of the battery, the heat pipe will be pumped into a vacuum state during the manufacturing process to reduce the boiling point of the working medium. Porous wick structures produce capillary effects on liquids which makes the liquid flow by itself combined with the surface tension of the liquid so that the working medium in the heat pipe can achieve the thermal circulation automatically. Heat pipes generally have two parts including evaporation section and condensation section (some special heat pipes also have an adiabatic section) [157]. When the evaporation section of the heat pipe is heated, the working medium is thermally gasified and flows to the condensation section under the action of small pressure difference. Then the gas phase in the condensation section becomes the liquid phase which returns to the evaporation section to complete the thermal cycle by the capillary action or its own gravity (the heat pipe is placed vertically or obliquely) [158] so that the heat generated by the battery is continuously transmitted to the external environment for the purpose of controlling battery temperature.

In the current research, the heat pipe commonly used in battery thermal management can be divided into sintered heat pipe [155,159], Loop heat pipe [156,160] and oscillating heat pipe [161,162].

4.1. Battery thermal management based on sintered heat pipe

Most of the evaporated section of sintered heat pipes are flat and contain capillary-shaped sintered wick structures on the inner wall, so they are more suitable for the thermal management of rectangular lithium batteries. Wang et al [163] designed a battery thermal management system based on sintered heat pipes for the thermal management of battery modules which contained 30 rectangular lithium-ion battery cells (simulated battery containers filled with atonal 324 which the thermal capacity is close to a real li-ion battery cell). As shown in the following Fig. 10, the condensing section of the heat pipe is fed into the flowing coolant to dissipate heat.

The test results showed that the surface temperature of each single cell can be controlled below 40°C when the heating power of each single cell was lower than 10W/cell, but the battery temperature can

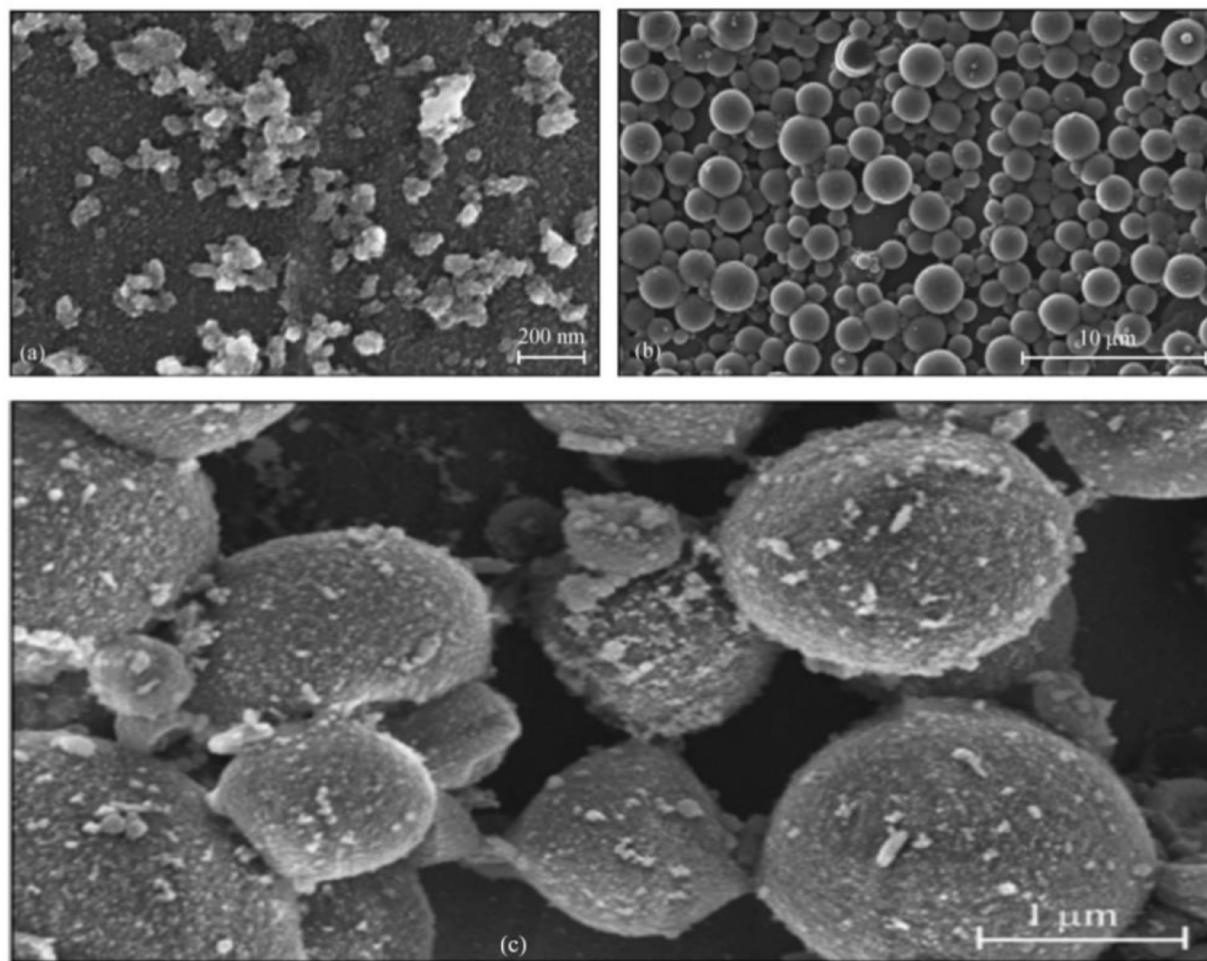


Fig. 9. Microstructure before and after adding nano titanium dioxide [154] (a) nano titanium dioxide, (b) PCM microcapsules (c) PCM microcapsules with nano titanium dioxide

only be controlled below 70°C when the heating power of single cell was 20–40W/cell. Rao et al [164] used electric heater to simulate the rectangular lithium-ion battery, and carried out similar research, too. It was found that the maximum temperature of the battery could be controlled below 50°C when the total thermal power of the simulated battery was less than 50W. Because two simulated cells are used in the experiment, the heat output power of each single cell was 25W, which showed that the experimental results were in good agreement with Wang et al [163].

Tran et al [165] cleverly used aluminum shell to wrap the side surface of cylindrical lithium battery module and used flat sintered heat pipe to conduct thermal management research. Using aluminum shell to wrap the side surface of the battery module can greatly improve the heating area of the evaporation section of the flat heat pipe and the fin structure of the condensation part can improve the heat transfer efficiency of the natural convection with the environment. The temperature of the battery can be controlled below 50°C. In addition, the experiment also studied the placement of heat pipe and found that vertical or horizontal placement of heat pipe was feasible and can work efficiently under different ramp conditions. To sum up, because of the capillary wick structure of the sintered heat pipe, the liquid working fluid can complete the process of reflux to the evaporation section under the capillary force without relying on the effect of gravity, thus avoiding the problem that the liquid working fluid of the heat pipe cannot return to the evaporation section under the microgravity condition. In addition, according to the experimental results of [165], as shown in the Fig. 10(b), the temperature of an electric heater with a

heat pipe placed at a slight angle from the vertical direction was slightly lower than that of an electric heater with a heat pipe with a slight angle away from the horizontal direction after 4000s. The possible reason was that the combination of capillary force and microgravity made the flow of liquid working fluid larger, which was conducive to the rapid transfer and diffusion of heat so that further improved the heat transfer efficiency of the heat pipe.

4.2. Battery thermal management based on loop heat pipe

The loop heat pipe is also an efficient phase change heat transfer device, as shown in the following Fig. 11(a), a typical Loop Heat Pipe (LHP) consists of an evaporator, a compensation chamber, a vapor transport line, condenser and liquid return line. Wick structures are located in the evaporator and compensation chamber, while the remaining loop components are made of smooth wall tubing, which can reduce the flow resistance of the working liquid that flows back to the evaporator. Moreover, an LHP has a separate evaporator and condenser, thus eliminating any entrainment effects that are likely to occur, and more heat can be carried. Consequently, LHPs are suitably used in power battery thermal management system [166].

Putra et al [156] used a box heater to simulate the heating of the battery, and tested the performance of the flat loop heat pipe as a heat exchanger in the thermal management system of lithium-ion battery for electric vehicles through experiments. The best performance of flat loop heat pipe can be obtained when the heat flux was 1.61W/cm² and produced a thermal resistance of 0.22 W/°C. When alcohol and acetone

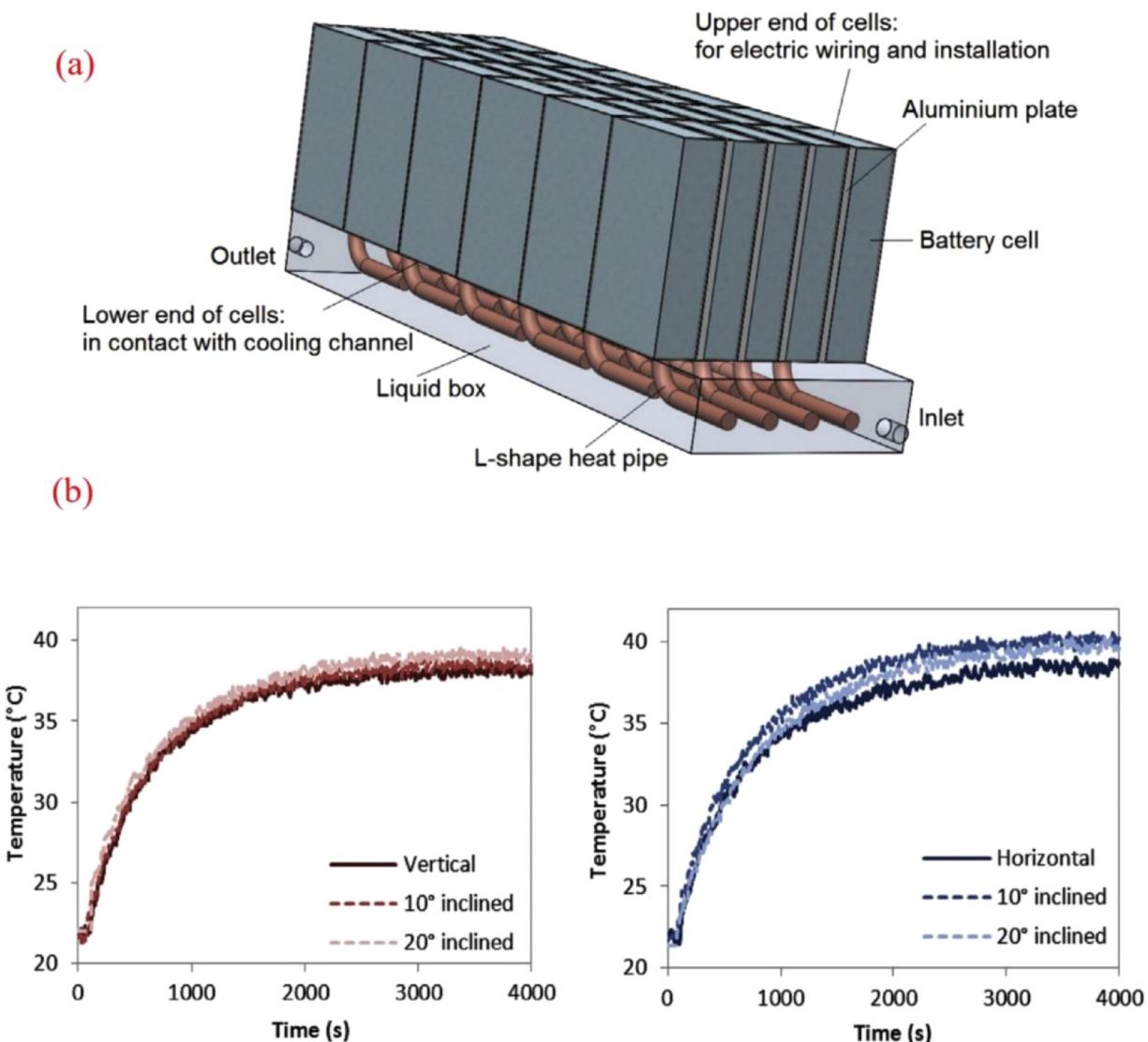


Fig. 10. (a) Battery thermal management based on heat pipes demonstration [163]; (b) Heater/heat pipes interface temperatures in various inclined positions under natural convection [165]

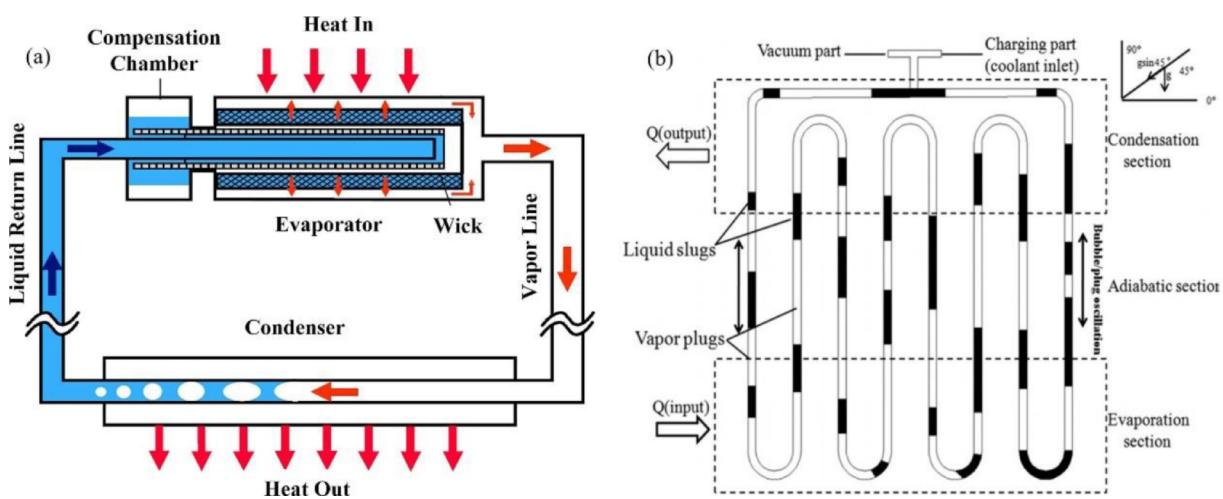


Fig. 11. (a) Schematic of loop heat pipes [166]; (b) Structure of oscillating heat pipes [157].

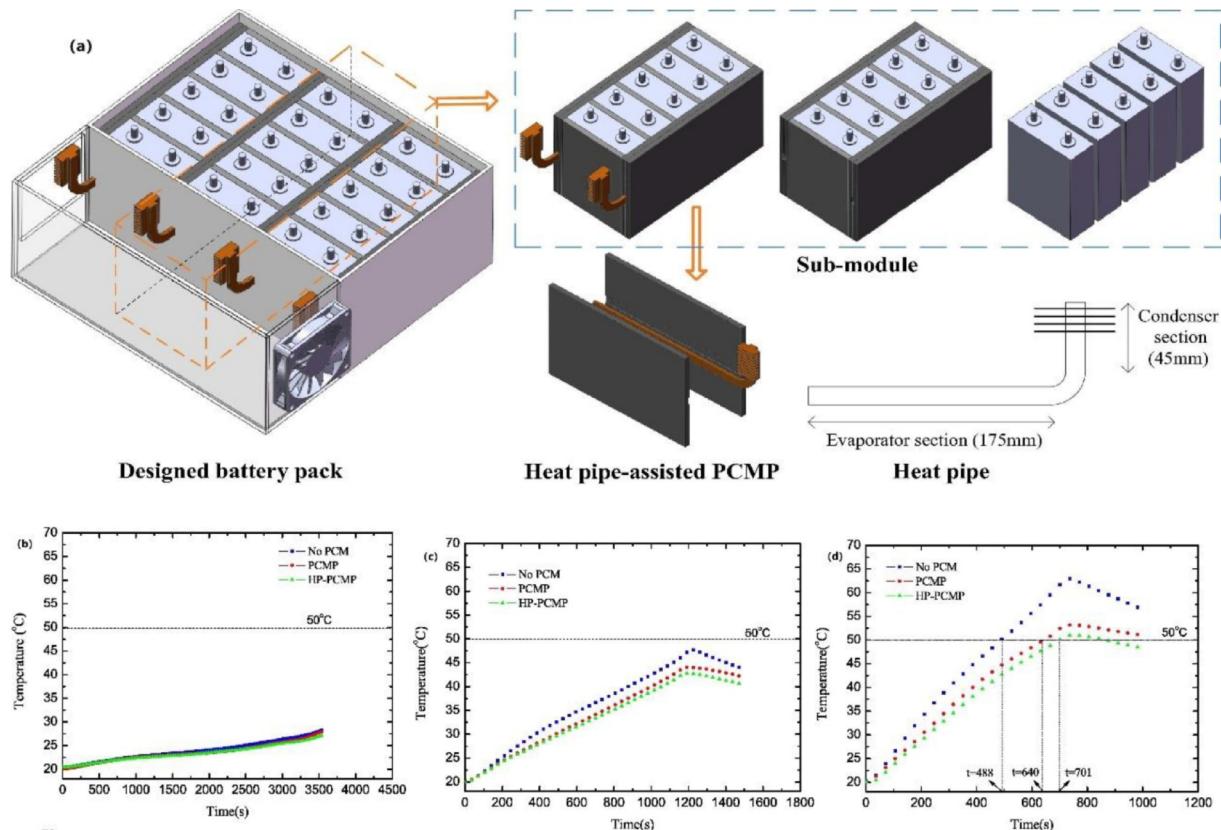


Fig. 12. (a) Schematic illustration of designed battery pack and sub-modules; (b-d) Temperature response of three modules under different discharge rates: (b) 1C, (c) 2C, (d) 3C [167].

were used as the working medium of the heat pipe, the maximum temperature of the evaporator was about 50°C, which was within the operating temperature range of ordinary lithium-ion batteries. Park et al [160,164] designed an optimized loop type heat pipe for cooling lithium-ion batteries on military aircraft. They used the finite difference method to analyze the heat transfer characteristics of the loop heat pipe in detail. The experimental results showed that the loop heat pipe can not only work well under the condition of changing heat load, but also keep the battery temperature at about 10°C.

4.3. Thermal management of batteries based on oscillating heat pipes

Oscillating Heat Pipe (OHP) can also be used in thermal management of power batteries which has been proposed and considered as a promising solution in a broad range of industrial and commercial areas owing to the simplicity, high performance and versatility [161]. The structure of the oscillating heat pipe is shown in the Fig. 11(b) above: it includes evaporation section, adiabatic section and condensation section. In a serpentine closed vacuum space composed of metal tubes, when the heating energy is applied to the evaporation section of the battery, the liquid vaporizes to produce bubbles, which expand and boost the pressure rapidly in the tube. Under the pressure of bubble, the working fluid flows to the condensation section with lower temperature, which shrinks and then breaks, resulting in pressure drop and working fluid reflux. In addition, the steam generated by heating evaporation and the liquid generated by condensation will form liquid slugs and vapor plugs in OHP randomly and spaced. Because of the pressure difference between the condensation section and the evaporation section as well as the pressure imbalance between the adjacent pipes, the working medium flows in the state of liquid-gas two-phase between the evaporation section and the condensation section so that achieving the heat transfer in the heat pipe [157]. It can be seen that

the internal oscillating power of the heat pipe is completely from the oscillating heat pipe itself. In the whole process, it does not need to consume other external power and complete the self oscillation process under the effect of thermal drive. Therefore, there is no capillary wick structure on the inner wall of their tubes in the manufacturing process to provide capillary adsorption force for liquid reflux.

Qu et al [161] studied the adiabatic section of the flexible oscillating heat pipe using deionized water as working fluid. Three flexible oscillating heat pipes were tested to evaluate the effect of the adiabatic section length and form on the start-up, evaporator temperature and overall thermal resistance of the heat pipe. The adiabatic section of Flexible Oscillating Heat Pipe (FOHP) was made of fluororubber tube with inner diameter of 4 mm and made into four shapes of "T", "ladder", "inverted U" and "n" respectively. They found that when the adiabatic section length of "T" FOHP was 570mm, 700mm and 870 mm respectively, and the power input was about 121W, 51W and 25W respectively, the evaporator temperature can be kept below 50°C. Wei et al [162] analyzed the influence of the working medium of the oscillating heat pipe on its heat transfer performance. In their work, a proof-of-concept plugin oscillating heat pipe with flat-plate evaporator and tube condenser has been developed and experimentally tested. In addition, the condensing section carried out forced convection heat exchange by setting a fan to convey air flow. The experimental results showed that when volumetric Filling Ratios (FRs) was 30%, 40% and 50% as well as pure water, ethanol and their different Mixing Ratios (MRs) (from 1:1 to 4:1) were used respectively, the average temperature of battery pack can be controlled below 46.5°C and the maximum temperature difference of battery pack was mostly in the range of 1, 2 °C under the input power of 56W. For such experimental results, they thought that the complementary characteristics of thermophysical properties of ethanol water mixture and temperature / concentration gradient mass transfer were the reasons for improving the performance of OHP.

4.4. Thermal management of batteries based on phase change materials and other structures combined with heat pipes

Although the application of heat pipes in the thermal management of batteries has achieved some results, there are still some shortcomings. In the study of Wang et al [163], when the heating power of a single cell was 20–40W / cell, the temperature of the cell can only be controlled below 70°C, which showed that the structure and materials of the sintered heat pipes cannot meet the requirements of high heat flow density environment. Furthermore, Rao et al [157] also pointed out that the thermal performance of OHP was influenced by its thermal resistance that decreased with the rise of the heating power which also showed that the heat resistance of the oscillating heat pipe was very large under the condition of high heat flux. In order to solve these problems, researchers [167,168] optimized the heat pipe based battery cooling system by setting fins in the condensation section of the heat pipes or introducing phase change materials in the area where the evaporation section of the heat pipe contacts the battery. Wu et al [167] installed straight fins in the condensation section of the sintered heat pipe and combined the optimized heat pipe with the thermal management system of the battery module based on the phase change material. The specific structure is shown in the Fig. 12(a) below. By the experiments, they found that the maximum temperature of the battery can be controlled below 50°C even under the maximum discharge rate of 5C, and the battery can achieve more stable and lower temperature fluctuation under the condition of charge and discharge cycles. In addition, they also set up corresponding comparative tests for battery packs without phase change materials and with phase change materials. The experimental results are shown in the Fig. 12(b-d) below. It can be seen that when the discharge rates are large, the PCM based battery thermal management system with fins and heat pipe structure has better heat dissipation performance.

Rao et al [169] also carried out similar experiments by using circular fins combined with sintered heat pipe and PCM. The results showed that the BTM system based on PCM had better control effect on temperature rise and temperature uniformity under the condition of natural convection. The maximum temperature of PCM/ Heat Pipe (HP)-based Battery Thermal Management (BTMS) can be controlled below 50°C for longer time than that of air-based BTMS and PCM-based BTMS. In addition, the maximum temperature difference (about 33.6%) can be significantly reduced by adding phase change materials into the module, while the maximum temperature difference can be further reduced by 28.9% by embedding HP into the phase change materials. The maximum temperature difference control time of PCM/ HP based BTMS under 5°C was longer than that of air-cooled based BTMS and PCM based BTMS. For some researches on the combination of oscillating heat pipes and PCM to enhance the heat dissipation of batteries can refer to [157,168].

4.5. Battery thermal management technology based on boiling cooling

The pool boiling and flow boiling of medium fluid is also an efficient cooling technology based on the principle of liquid-gas phase change, which has great potential in the thermal management of electronic components [170] and this technology can also be used in the field of battery thermal management [171–174]. For the first time, Dutch scholar R.W. van Gils et al [171] innovatively proposed the method of cooling single cell by boiling with liquid (Novec 7000, which contains 99.5% hydrofluoroether) and carried out some relevant experiments. Novec 7000 is kind of dielectric coolant, and is also stable at high temperature, non-flammable and environmentally friendly. The boiling temperature of Novec 7000 is 25–40°C which is within the optimal operating temperature range for lithium-ion batteries [172]. The experimental schematic diagram is shown in the Fig. 13 below. Through experiments, they explored the dielectric properties, cooling capacity and the ability of the boiling process to thermally homogenise batteries.

The experimental results showed that the cooling performance of Novec 7000 was much higher than that of air when it was used as boiling medium and its thermal stability can be maintained even when it was used for cooling batteries.

Maan et al [173] proposed a phase change cooling system based on pressurized propane for temperature management of lithium-ion batteries for hybrid electric vehicles. By studying the liquid level of propane in the battery pack, they found that the saturated liquid propane only covered 5% of the total length of the battery at the pressure of 8.5 bar, keeping the maximum temperature of the battery below 39°C for 600s in the high rate charge discharge cycle at 7.5C. Furthermore, the longer the propane covered cell is, the lower the maximum temperature the cell reaches. Covering 30% of the battery length with saturated liquid propane can even keep the temperature below 34°C. However, the application scope of the system is relatively narrow and this work does not explore the corrosion of propane to the battery.

Furthermore, some inorganic liquid such as liquid ammonia can also be used as the boiling cooling medium. In the study of Maan et al [174], the design scheme of PCM battery thermal management system with liquid ammonia as a novel phase change material was proposed. Based on the high heat transfer coefficient of pool boiling, the cooling system coupled the natural convection with the liquid ammonia which directly contacted with the battery for boiling to enhance the heat transfer. The results were encouraging that it was able to maintain the maximum temperature of the battery below 33°C when only 5% of the battery front surface is covered with a boiling ammonia pool. Furthermore, increasing the area covered by the pool can reduce the maximum temperature and improve the temperature uniformity of the battery. However, the scope of application of the system is also relatively narrow, which is only applicable to hybrid vehicles using ammonia as carbon free fuel in the future. In addition, the leakage of ammonia will pollute the environment to a certain extent as well as the direct contact between liquid ammonia and battery may cause corrosion. Therefore, the author suggested that in the future research, the liquid ammonia can be placed in the cooling plate made of high heat conducting metal to indirectly contact with batteries to solve the above problems [174].

In addition to the flow boiling, An et al [172] explored the effect of flow boiling of Novec 7000 in mini channel on the heat dissipation of batteries. They conducted experiments at different battery discharge rates as well as fluid Reynolds number and found that the battery thermal management system based on hydrofluorane flow boiling in mini channels had a good cooling effect. When the heat transfer mode was mainly boiling heat transfer, the battery temperature can be maintained at about 40°C. On the other hand, due to the advantage of boiling heat transfer, the maximum surface temperature difference of cell can be effectively reduced to about 4°C. By using HFE-7000 as working medium, Wang et al [175] analyzed the temperature distribution and boiling characteristics of the cells in the battery module at different inlet temperature, flow rate as well as inlet speed. The thermal management module is shown in the Fig. 14(a). Through the computer simulation results, it can be found that the heat flux density on the cell wall is low when the cell is discharged at a low rate, and the low temperature makes most of the working medium liquid. The working medium showed a better advantage in reducing the maximum wall temperature of single cell under this single-phase flow. On the other hand, the high temperature caused by the high heat flux on the cell wall made most of the working medium in the vapor-liquid two-phase state. In contrast, the working medium has more advantages in improving the temperature uniformity of the battery pack under the condition of two-phase turbulence. The computer simulation results are shown in Fig. 14(b-g), and the experimental results are consistent with the simulation results.

4.6. Summary

In this chapter, the commonly used battery thermal management

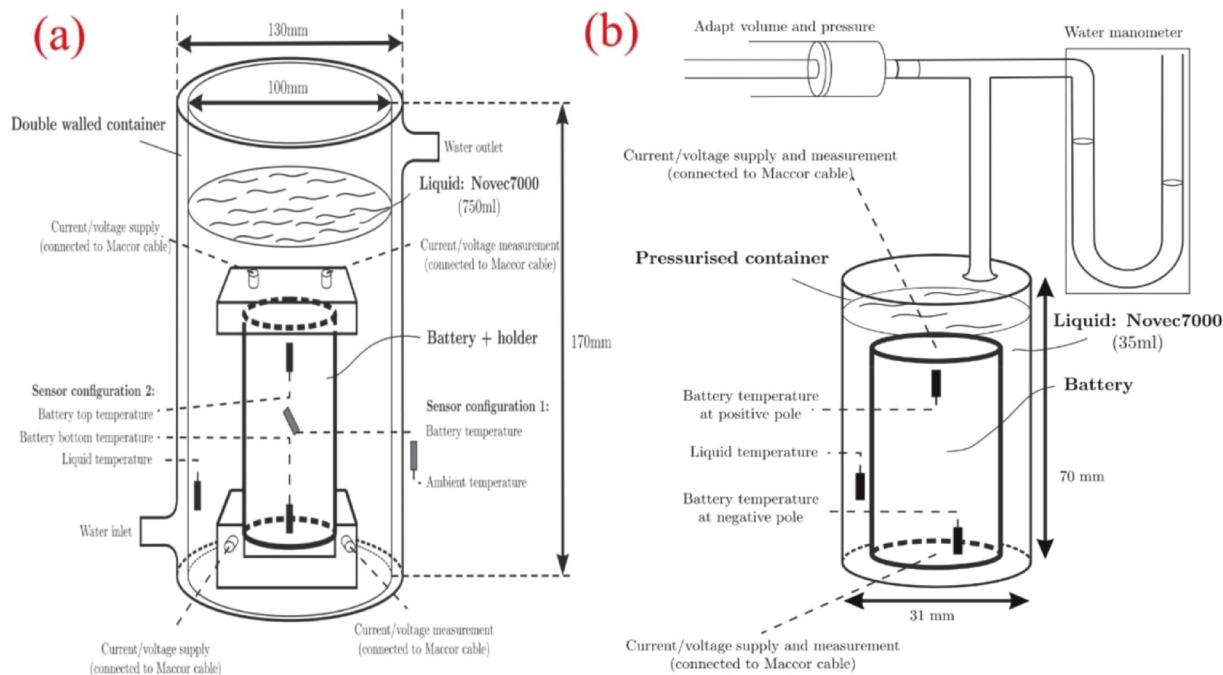


Fig. 13. (a) Experimental diagram of Setup 1 and (b) experimental diagram of Setup 2 [171].

technology based on the principle of liquid-gas phase transition is introduced. For heat pipes, there are three types of heat pipes that can be used for battery thermal management. When the evaporation section of heat pipes is in the condition of low heat flux, the thermal management module can control the battery temperature within a reasonable range only by heat pipe. However, in the case of high heat flux, the heat absorbed by the liquid-gas phase transition process of the working medium in the heat pipe is not enough to control the temperature of the battery. Therefore, it is necessary to improve the original passive thermal management system. In addition to the optimization of heat pipe structure, it is necessary to combine with other thermal management methods, such as adding solid-liquid phase change materials or introducing active thermal management system for coupling. One of the common methods is that setting solid-liquid phase change materials between the evaporation section of the heat pipes and the batteries to strengthen the absorption of heat during the phase transition process. At the same time, the condensation section of the heat pipe can be improved by setting the fin structure and when necessary, the heat in condensation section can be transferred by forced convection or by cold fluid. On the other hand, the flow path of coolant can be set in many ways, it can be set not only outside but also inside the passive thermal management module as shown in Fig. 15 below.

In fact, the novel thermal management system based on the combination of passive thermal management system based on solid-liquid phase change materials as well as heat pipes and active thermal management system based on liquid cooling is a relatively efficient thermal management system at present. Although a single passive thermal management system can store the heat generated by the battery in the form of latent heat inside the phase change material, in the case of high heat flux, if the stored heat cannot be transferred to the external environment in time, the phase change material will eventually liquefy or vaporize completely to lose the ability of thermal management of the battery. By coupling the above active thermal management system, the heat transfer rate of the passive thermal management system to the outside world can be increased, and its working cycle ability can be further guaranteed. In addition, the research focus of pool boiling cooling is mainly focused on the choice of cooling medium and the contact mode between cooling medium and batteries. However, pool

boiling cooling is mainly applied to hybrid electric vehicles at present, and the future research focus can focus on the application of boiling cooling to battery thermal management of pure electric vehicles. Based on pool boiling heat transfer, flow boiling heat transfer strengthens the convective heat transfer with the batteries, which is also a heat management method that can be put into more research in the future.

5. Comparison of various battery cooling technologies and discussion of cost-effectiveness

In this paper, the recent battery thermal management technology based on phase transition principle is introduced in detail. Compared with the traditional air cooling and water cooling, the introduction of phase change materials does not need to consume additional fan power or pumping power, which is a pure passive thermal management mode. Due to the problem of low thermal conductivity of pure phase change materials, most of the current researches are strengthened by adding high thermal conductivity materials. According to the existing research results, the thermal conductivity of phase change materials can be improved by 33.8% - 250% [112,117,119,120,122], among which the metal nano materials are more significant. Secondly, the latent heat and melting point of the composite phase change material are little compared with the pure phase change material due to the low amount of addition. However, due to the high cost of nano materials, it is not suitable to popularize all electric vehicles considering the manufacturing cost and improving effect.

Using metal foam as enhanced material, the thermal conductivity of pure phase change material can be increased to the original 411%-21824% [40,126,148]. In the three commonly used metal foams, the effect of aluminum foam is the best, which is attributed to its higher thermal conductivity. In addition, due to the porous characteristics of metal foam, the molten liquid phase change material will be adsorbed by capillary force, which can maintain the stable morphology of phase change materials. The thermal conductivity of the composite phase change material can be increased to 11.2 (W/m·K) [139] by adding expanded graphite into paraffin. Compared with paraffin, the thermal conductivity is increased by nearly 5500%, but the latent heat of phase change material is greatly reduced due to the large amount of expanded

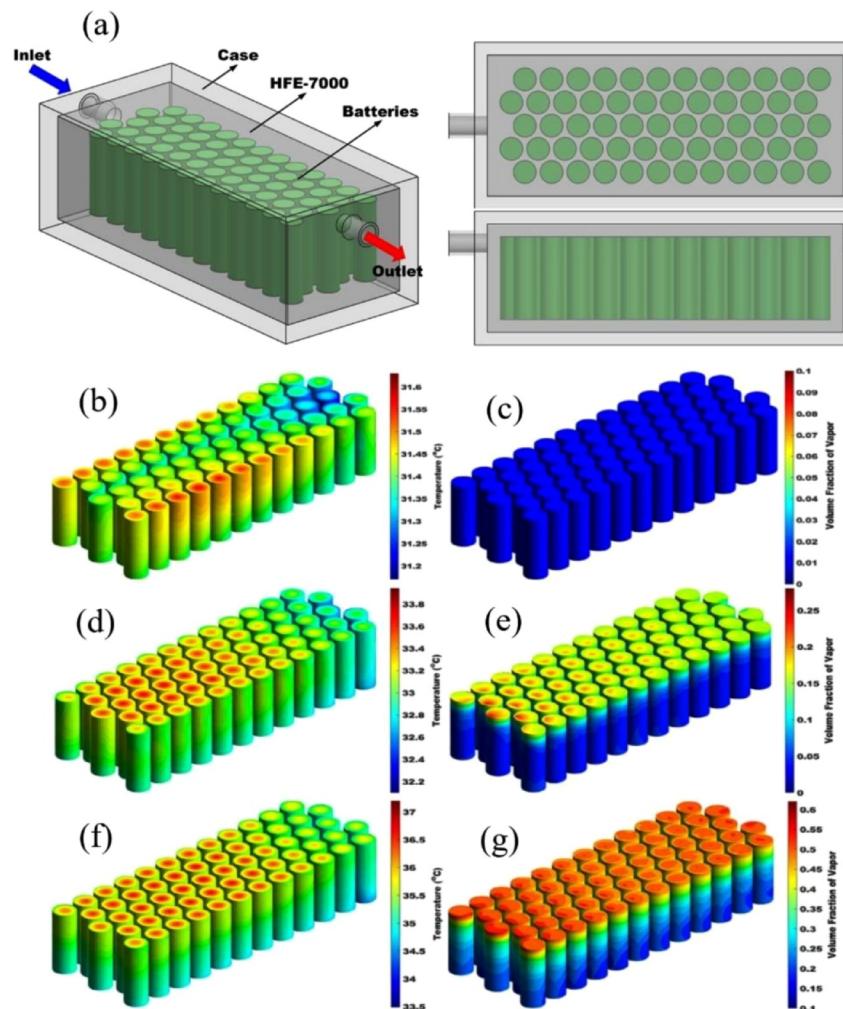


Fig. 14. (a) Schematic illustration of the thermal management module; (b-g) Flow boiling heat transfer characteristics of the HFE-7000-based BTMS at different discharge rates: (b) temperature distribution at 1C, (c) vapor volume fraction at 1C, (d) temperature distribution at 3C, (e) vapor volume fraction at 3C, (f) temperature distribution at 5 C, (g) vapor volume fraction at 5C [175].

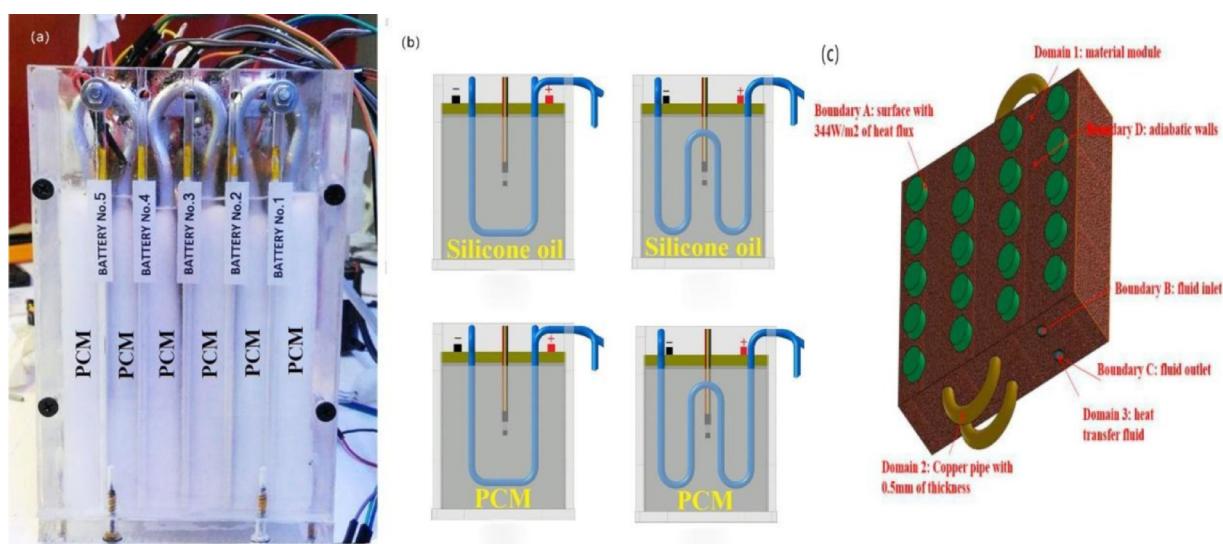


Fig. 15. Physical graphic of experimental device (a); Different types of flow path in hybrid thermal management system (b, c) [13,176].

graphite. According to the existing research, the composite of expanded graphite and paraffin is made by adding graphite powder into the melted paraffin stirring evenly and then obtained after the paraffin solidified. The metal foam can be directly embedded into the melting phase change material, and it will be removed after the phase change material solidified. In addition, the manufacturing cost of the porous material is low, and the composite method with pure phase change material is relatively simple. During the manufacturing process, the composite material with ideal thermal conductivity and phase change latent heat can be prepared by adjusting the porosity and pore diameter of the material, which can be popularized in electric vehicles.

In the process of metal mesh and metal fin compounding with paraffin, expanded graphite is usually added to stabilize the morphology of phase change materials, after the introduction of the above materials, the thermal conductivity of paraffin can be increased by 763%-2842% [9,123], and the change of latent heat is small. In addition, the combination of metal mesh and metal fin with paraffin is only simple embedding. Combined with its low manufacturing cost, this kind of composite phase change material is also worthy of promotion and application in battery thermal management. Graphene is also a kind of high thermal conductivity material, which can enhance the thermal conductivity of pure phase change materials to 25 (W/m·K) [147], which is 12400% higher than paraffin. However, due to the high manufacturing cost of graphene, it is generally possible to add appropriate amount of graphene to other low-cost high thermal conductivity materials to further improve the thermal conductivity of materials, and then can be applied to some specific electric vehicle. For high thermal conductivity and high resistivity materials with insulation effect, the thermal conductivity of the composite increases by 1072%-2050% compared with paraffin [98,111]. In view of its relatively moderate cost, it can be widely used in the case of high discharge voltage. In addition, similar to the metal nanomaterials, due to the higher density compared with paraffin, the additives are prone to deposit when the paraffin melts, which limits its application.

The application of heat pipe makes the pure passive battery thermal management mode have a new choice. The manufacturing cost of heat pipe is low, and it has good sealing performance. In addition, when the heat flux of battery surface is low, only heat pipe can effectively control the temperature of batteries, which can be widely applied in some small electric vehicle fields. When the battery surface has high heat flux, only passive thermal management cannot effectively control the temperature of the batteries. Although the active liquid cooling method can effectively deal with the above situation, the pumping power of driving the coolant to flow and heat transfer cycle will also increase. In the long run, from the perspective of economy, the loss of additional work is tremendous. The combination of active and passive is beneficial to reduce the loss of additional work. Adding active thermal management system to the passive thermal management system based on solid-liquid phase change material or heat pipe can effectively strengthen the heat exchange between the passive thermal management system and the external environment. On the other hand, most of the heat generated by the battery is stored by the passive thermal management system in the form of phase transition latent heat, which can be called the passive thermal management system plays a leading role. The application of active thermal management system can relieve the heat storage pressure of passive thermal management system and play an auxiliary role. But the active liquid cooling method is mainly through the convection of the coolant. Therefore, compared with the pure liquid cooling active thermal management system, the additional power loss of the active combined with passive thermal management system is relatively small, which belongs to a relatively lower cost thermal management mode. However, this kind of active and passive thermal management system is more complex, with the increase of some auxiliary equipment, the load of electric vehicle will be increased accordingly.

Boiling cooling is a novel thermal management method in recent years. According to the existing research results, part of the battery

thermal management system based on boiling cooling can effectively reduce the maximum temperature of the battery and the temperature difference of the single cell in the battery module. Most boiling coolant is harmful to human body, so it has relatively high requirements for sealing, and the corresponding technical cost will be increased. This technology is still in the research stage, and its commercial application is not mature.

6. Conclusion and future prospect of corresponding technology

In this paper, the current research status of lithium-ion battery is reviewed in detail, which is based on the mathematical modeling method to predict the temperature field of the battery under different working conditions and based on the phase-change technology for the thermal management of the battery. However, there are still some challenges in these technologies, which need to be improved to overcome these shortcomings. The main conclusions and challenges are presented as follows:

- (1) The calculation time of Laplace transformation and polynomial approximation is reduced to a certain extent, but the calculation accuracy is lower than other models. By comparison, the Galerkin's method is an ideal method for simplification of order reduction. Furthermore, after comparing SMP, SP, MP and ESP, it can be seen that SMP model is more suitable for occasions with higher calculation accuracy.
- (2) For the eutectic hydrated salt, the enthalpy of phase transition and specific heat capacity can be significantly increased by adding TiO_2 nanoparticles. Compared with paraffin wax, the noncorrosive organic hydrate TME has higher thermal conductivity and is non-combustible. But limited by the solubility of water to TME, the further promotion of the dissociation heat of TME hydrate is also limited.
- (3) Due to the high cost of nano materials and graphene, it is difficult to popularize and apply them in electric vehicle. Powder additives are prone to deposit after several solid-liquid phase transition cycles, which will affect its strengthening performance. Expanded graphite, metal mesh, metal foam and metal fins have lower cost and can improve the thermal conductivity of pure phase change material significantly. But the risk of electric leakage of the whole battery module also increases.
- (4) Hybrid BTMS can meet the thermal management needs at high heat flux but this also increase the weight, complexity and additional power consumption. Nanofluids [11,126,177,178] used in active thermal management module of the hybrid BTMS as coolants are far from meeting practical application because of the high viscosity, imperfect thermal conductivity as well as instabilities.
- (5) Part of the battery thermal management system based on boiling cooling can effectively reduce the maximum temperature of the battery and the temperature difference of the single cell in the battery module. Most boiling coolant has relatively high requirements for sealing, and the corresponding technical cost will be increased. This technology is still in the research stage, and its commercial application is not mature.

In the future, more attentions should be paid on following three aspects:

- (1) For inorganic phase change materials with high thermal conductivity and nonflammability, they are corrosive in melting state, which greatly limits their application in thermal management of batteries. In the future, more research can be put into thermal management by indirect contact between thermal management module and battery module based on the combination of inorganic phase change materials and high thermal conductivity materials. Furthermore, there are few researches on the application of hydrate

- phase change materials in the thermal management of batteries, and it is also worth more research in the future.
- (2) Although PCM capsule has some challenges in manufacturing difficulty and cost, it still has a good application prospect. At present, most PCM capsules are made of organic polymer materials, which makes the stability of the capsule poor. In the future, flexible inert metal materials can be considered to prepare PCM capsule shell to overcome the above challenges.
 - (3) The conventional high thermal conductivity nanofluids, which are expected to be used in hybrid thermal management systems, have the disadvantages of unsatisfactory thermal conductivity and high viscosity. High viscosity of liquid can consume more pumping power, while poor thermal conductivity can reduce the heat transfer efficiency between active and passive thermal management systems. In the future, more research can be devoted to reduce the viscosity of nanofluids and further promote their thermal conductivity.

Declaration of Competing Interest

The authors declare that they have no conflict of interests regarding the publication of this paper.

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