Chapter 2

Experimental and Numerical Studies on Phase Change Materials

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Additional information is available at the end of the chapter

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Abstract

Phase change materials (PCMs) are attracting significant attentions in research and application, categorized into mainly three types, that is, organic (O), inorganic (IO) and eutectic (E). This section introduces the experimental and numerical investigations conducted in recent decades, mainly focused on the properties enhancement of PCMs and the performance improvement of its application in latent heat storage (LHS) units, as well as the evaluation and optimization of LHS units. It was concluded that lots of contribution have been made to PCMs and LHS units analysis. However, there is still some weakness in research, such as the lackness of detailed and systematic research on properties, the non-uniform standard on testing method as well as the contradictory conclusions. The most evaluation of LHS units is based on energy, instead of exergy, entropy and entransy. There is another issue that most of the research is based on numerical analysis, while less experimental research is conducted, especially in the case of LHS unit.

Keywords: phase change materials (PCMs), latent heat storage (LHS), numerical, experimental

1. Introduction

Energy is the basis of modern society and is important for the survival of mankind as well as the development of civilization. Non-renewable and renewable sources are two kinds of energy source. Since the non-renewable energy source will be run out someday, the utilization of renewable energy source has been paid more and more attention in research. However, in most cases of renewable energy sources, such as solar and wind, intermittent nature is found. What is more, there is always a gap between energy supply and energy demand, as far as power, space and time in concern. Thus, energy storage technologies are proposed to solve or diminish this issue.

Energy is usually stored in energy storage (ES) system, in the form of mechanical, chemical, biological, magnetic and thermal. These energy storage forms can also be subsidized further in details. For instance, mechanical energy can be stored in compressed air, flywheel or hydro-pool, etc. and chemical energy can be stored in battery, reversible-reaction or hydrogen, etc. Among these energy storage forms, the most commonly used is the thermal energy storage (TES) with phase change materials (PCMs), due to its merits of low-cost, environmental-friend, easy-to-operate and abundant sources of storage facilities.

As a matter of fact, we human being has used renewable energy and conducted thermal energy storage, since quite a long time ago. For example, the ancient people utilized wind or hydro power to drive wheels for irrigation and they collected ice or snow in winter for cooling in summer. In modern society, we try to fully utilize the clean energy source, to deeply understand the process involved in TES process and to seek nature materials or manufacture artificial materials for TES. For the performance improvement of TES, the thermophysical properties are important limitations. For instance, the limited thermal conductivity of PCMs strongly constrains the conductive heat transfer process. The viscosity of PCMs at liquid phase also constrains the convective heat transfer process. In this section, we will introduce some progress of the research on PCMs and TES and discuss on the weak points.

2. Experimental studies of PCMs

Experiments studies were conducted on the properties of PCMs and the performance in LHS, as well as the enhancement.

2.1. Types and properties of PCMs

The materials involved in LHS are called as phase change materials (PCMs). There are varieties of PCMs under development, categorized as organic (O), inorganic (IO) and eutectic (E) materials, available in a wide range of melting/solidification temperature (**Figure 1**).

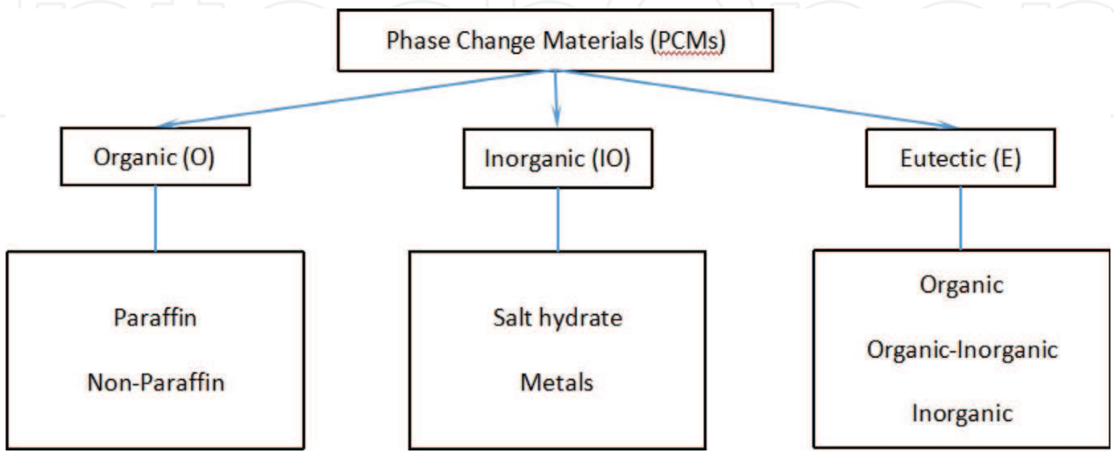

Figure 1. Categories of PCMs.

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Thermal properties	**Physical properties**	**Kinetic properties**	**Chemical properties**	**Economic availability**
High latent heat of transition	Small volume change	Sufficient crystallization rate	Long-term chemical stability	Abundant
High thermal conductivity	Low vapor pressure	No supercooling	No toxicity	Cost effective
Suitable melting/ solidification temperature	High density		Non-flammable	Available
			Non-corrosive	Commercially viable

Table 1. Properties of PCMs in demand.

Desired property of PCMs includes thermodynamic, kinetic, physical and chemical properties, as well as economic availability, as shown in **Table 1**.

Unfortunately, there is not a single kind of PCMs that satisfies all the properties listed above. The most undesired character of PCMs property is its thermal conductivity, since it will limit the heat transfer during energy storage/release process and correspondingly lead to deteriorated performance of LHS unit. This is often the case, except for some metallic PCMs. For instance, several measures have been taken. The major technical method is to composite with materials of high thermal conductivity.

2.2. Types of TES

TES can be categorized as three types, that is, sensible heat storage (SHS), latent heat storage (LHS) and thermo-chemical storage (TCS). In the first type (SHS), thermal energy is stored as the temperature increase of certain matters, usually with large thermal capacity. So, the amount of energy storage Q can be easily estimated as the product of mass m, thermal capacity C and temperature uplift ΔT, as shown:

$$Q = \int_{T_1}^{T_2} m \cdot C \cdot dT \tag{1}$$

In the second type (LHS), thermal energy is stored as the phase change process of certain materials, including the transformation of phase between solid and liquid (S-L) in melting/ solidification process, between solid and gas (S-G) in sublimation/desublimation process, from liquid to gas (L-G) in condensation/evaporation process, as well as the transition from one solid phase to another (S-S). The amount of energy storage Q is the sum of the sensible heat stored in both phases and the latent heat involved in phase-transformation, which is the main portion of energy storage amount.

$$Q = \int_{T_1}^{T_m} m \cdot C_{phase\_1} \cdot dT + m \cdot \Delta H_m + \int_{T_m}^{T_2} m \cdot C_{phase\_2} \cdot dT \tag{2}$$

In the third type (TCS), thermal energy is stored in similar way as LHS. The major difference is that thermal energy is mainly stored as the enthalpy change in thermo-chemical reaction, instead of phase-transformation process.

Comparing with LHS and TCS, SHS technology often requires larger vessels. Comparing with LHS, TCS is associated with larger energy storage density, but is still at pre-mature state in terms of research and development. Therefore, latent heat storage (LHS) attracts the most attention in research and is believed as the most promising technology.

The performance of heat storage/release in PCMs is realized in LHS unit. The major favored characteristics of LHS unit includes faster rate of heat charging/discharging, higher efficiency of heat release, based on thermodynamic evaluations, including the basis of energy, exergy, entropy and entransy as well. Another important research field is the optimization of LHS unit.

It is widely accepted that performance of LHS unit is mainly constrained by heat transfer process. Therefore, heat transfer enhancement is a major task for LHS unit performance improvement in most research. Since heat transfer is generously expressed as:

$$Q = K \cdot A \cdot \Delta T_m \tag{3}$$

where K represents the heat transfer coefficient in conduction or convection process, A represents the surface area for heat transfer and ΔT_{m} represents the temperature difference between PCMs and HTF. The enhancement of heat transfer implies the increase of Q. So, it is obvious that there are three major methods for heat transfer enhancement of LHS unit, that is, increase of K, A and ΔT_{m}.

The heat transfer coefficient should include both conductive and convective. The increase of conductive heat transfer coefficient can be mainly traced back to the thermal conductivity enhancement on PCMs. The only exception would be the encapsulation of PCMs. As far as the increase of convective heat transfer coefficient, the theoretical basis is convective heat transfer. Therefore, the progress on convective heat transfer can be applied directly in the performance improvement of LHS unit, such as the influence of passage size and shape, the effects of faster flow velocity and the disturbed flow pattern. More effective increase of convective heat transfer coefficient should be attributed to the application of heat pipe (HP) technology.

2.3. Heat transfer enhancement techniques

Heat transfer for thermal energy storage applications with phase change materials is reviewed by Ref. [1]. The major measures include conductive heat transfer enhancement and convective heat transfer enhancement.

2.3.1. Composites with porous materials

Composite with porous materials is an effective method for thermal conductivity enhancement of PCMs. Impregnation is a fast-growing technology. The porous material offers space for PCMs and the high thermal conductivity of porous materials supports more effective heat transfer in composite. Expanded graphite and metal foam are the mostly adopted porous materials.

Zhao and Wu [2] reported the considerable improvement of thermal conductivity of sodium nitrate with porous expanded graphite matrix and metal foams. The experimental results of embedding non-metallic PCMs in porous graphite showed tens or hundreds times of thermal conductivity improvement. Siaphush et al. [3] reported the effective thermal conductivity increased from 0.423 W/m/K to 3.06 W/m/K, when 95% porosity copper foam is adopted in PCMs of eicosane. It is also reported that critical porosity value exists for enhancement with porous carbon graphite foams. Yin et al. [4] reported in experiments that the critical mass fraction of porous graphite is 6.25%. Exceeding this value, the reinforcement effect decreases. Similar phenomenon is also found in our research on the effect of adoption expanded graphite in octadecane for performance improvement of LHS unit. However, the critical value is found at around 20%. Gao et al. [5] investigated the thermal performance of a direct contact thermal energy storage container with erythritol and expanded graphite. The thermal conductivity is reported as increased by about 2.5 times, with 4% mass fraction of EG, and the melting time is reduced by 16.7%.

Comparing with the amount of porous materials in composite, it is also reported that the pore structure is more important for composite. Lafdi et al. [6] investigated experimentally on the effects of foam porosity and pore size on the melting rate of PCMs. Zhong et al. [7] reported that small pore size and thick ligament in graphite foam leads to higher thermal diffusivity, while large pore size and thin ligament leads to larger latent heat storage capacity. Since the thermal diffusivity and latent heat storage density are both important factors, the pore size and ligament should be optimized in the design of LHS unit. Wu and Zhao [8] reported that mixed porous base is more effective than single porous base. Zhang et al. [9] studied the performance of metal foam (copper) and paraffin composite. Gulfam et al. [10] investigated the enhancement of thermal conductivity with expanded graphite in paraffin wax. Teppei et al. [11] reported high thermal conductivity of erythritol enhanced with porous nickel. Similar works are also reported by Nomura et al. with metal-stabilized carbon-fiber network [12] as well as expanded perlite, diatom earth and gamma-alumina [13].

Besides expanded graphite and metal foams, ceramic is also adopted recently as enhancement medium, as Li et al. [14] reported. With the development of material science, there should be more materials with porous structure, such as graphene, aerogel, etc., under consideration for the enhancement of thermal conductivity as well as other properties.

2.3.2. Dispersion of high conductive particles

The effect of addition of metal particles, especially with nano-size, on the enhancement of thermal conductivity of PCMs is also reported widely. Different from the obvious and established structure of compressed expanded graphite and metal foam, the distribution of particles are more like to expanded graphite in composite. However, the effects are usually better in the case of nano-particles addition. The reinforcement effect by the dispersion of nano-particles in continuous PCMs should be attributed to the unique phenomenon at microscopic scale, for example, reduce the internal resistance for heat transfer, which is also reported for the thermal conductivity enhancement of heat transfer fluid (HTF) in literatures.

Fan et al. [15], Qi et al. [16], Tao et al. [17], Kim et al. [18] and Shi et al. [19] investigated the effects of several types of carbon-based nano-particles. It is found that disk carbon nano-particles can improve the thermal conductivity by 10 times. Besides graphite or graphene, carbon nanotubes (CNTs) are more typical nano-particles in composite. Zhang et al. [20] investigated on nanoscale heat transfer in composite of sugar alcohol and carbon nanotubes. It is reported that specific improvement of heat transfer depends on the material and the diameter of CNT. Carbon nanofibers (CNFs) are another common nano-particles in composite. Fereshteh et al. [21] analyses the application of phase change material with carbon fibers for thermal management of a Li-ion battery cell. It is concluded that the application of carbon fibers influences the temperature distribution in cells. Higher concentration of carbon fibers leads to more uniform temperature distribution. The maximum thermal conductivity enhancement degree is reported as 115% and averaged at 105%. Nomura et al. [22] reported a significant reinforcement degree of thermal conductivity for erythritol. Different CNFs groups and its mixture are adopted. It is found that with the mixture of CNFs at different length, thermal conductivity is more enhanced, comparing with the addition of single CNFs. To further construct the network for heat transfer inside composite, low-melting metal, such as indium is added to help bridge CNFs nearby. In recent studies, other carbon materials are under research.

Besides the carbon materials, the addition of nano-metal-particles, such as Cu, Ti and other magnetic metals, in composite are also conducted by researchers Kibria et al. [23], Zhang et al. [24], Luo et al. [25], etc. It is concluded that the thermal conductivity is enhanced, and sometimes the thermal capacity is also enhanced. Mettawee et al. [26] reported the effect of Al powder on thermal conductivity enhancement of paraffin wax. Motahar et al. [27] reported non-monotonic behavior of thermal conductivity, and optimum value of nano-particles occurs in composite. Wang et al. [28] reported the increase of thermal conductivity with mass fraction of CNTs. Similar result of MWCNTs is also reported by Zeng et al. [29] for palmitic acid. Oya et al. [11] studied the thermal conductivity enhancement of erythritol with graphite and nickel particles. The largest enhancement is reported as 6.4 times higher, comparing with the thermal conductivity of pure phase change material, at 15% volume fraction of expanded graphite. Khyad et al. [30] adopted 1% mass fraction of aluminum or copper to enhance thermal conductivity of paraffin.

Since the nano-particle can enhance the thermal conductivity of PCMs with the similar mechanism, more research is expected on this scope, with the development of materials science on materials as well as the manufacture method.

2.3.3. Using extended surface

Surface area for heat transfer is the most common method applied for the heat transfer enhancement of LHS unit, mainly in the form of fin-structure. The adoption of fins increase the contact surface between HTF and PCMs. Research is mainly focused on the selection of fin materials as well as the configuration and number of fins in LHS unit. As far as fin materials are concerned, thermal conductivity, density, cost and corrosion as well as mechanical performance are major concerns. Recently, mostly metal, such as copper, bronze, steel, stainless steel, aluminum alloy, etc., and sometimes graphite or ceramic are used as fin materials.

The core of fin-structure is its configuration, including shapes and orientation. The performance of single structured-fin will lead to the number of fins in demand is influential to the configuration of fins in LHS unit. The investigation of fin configuration is similar to heat exchanger (HE) with almost constant temperature boundary. The typical structure of LHS unit is tube-and-shell. So, there will be two forms of PCMs arrangement, that is, inside of tube and outside of tube as well as annual space between tubes.

As far as the orientation of fins is concerned, there are two mainly forms, that is, alongside and perpendicular to the axial direction. The fins can be arranged inside and outside of tubes (**Figure 2**).

Sparrow et al. [31] experimentally investigated the solidification process of PCMs in a finned vertical tube. It was concluded that conduction controls the process, when liquid temperature is lower and at melting temperature. While convection is the controlling mode for temperature above melting temperature. Tao et al. [32] investigated numerically with the performance of LHS unit in a photo-thermal (PT) application. Velraj et al. [33] reported with numerical and experimental analysis on vertical finned tube. The results show the reversal decrease of solidification period with number of fins. Zhao and Tan [34] investigated the effects of HTF temperature and flowrate as well as fin height on the charging rate of LHS unit. It is concluded that with the increase of HTF inlet temperature and mass flowrate, as well as the increase of fin height, the charging period is shortened, implying enhanced heat transfer process. Erek et al. [35] analyzed the effects of fin parameters, such as fin size and fin space, as well as the effects of HTF on the dimensionless energy storage value. Liu et al. [36] conducted similar experimental research on the melting of stearic acid in annual space. It is concluded that heat conduction and natural convection are both the factors for heat transfer enhancement in LHS unit. Hosseini et al. [37] concluded that with the increase of fin's height, the reduction of melting

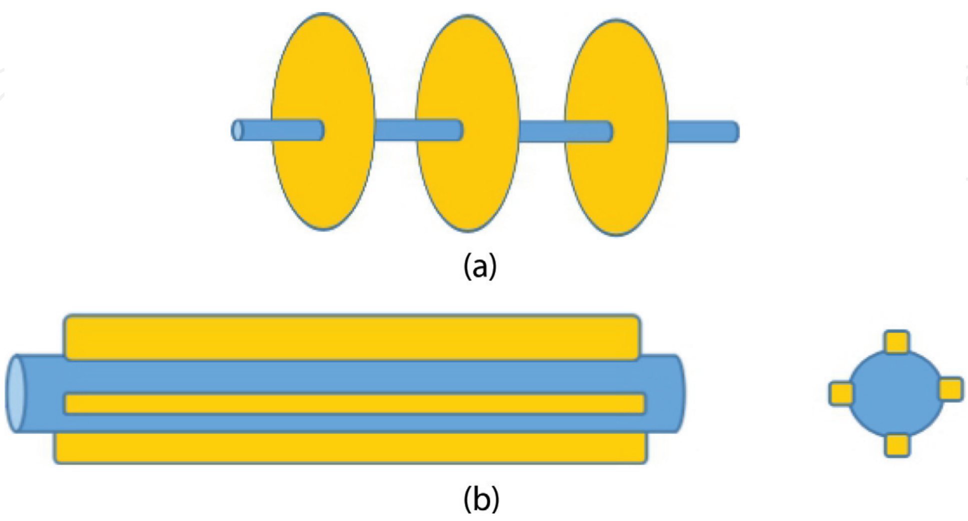

Figure 2. Sketch of fin configurations. (a) Perpendicular to the axial direction and (b) alongside the axial direction.

time exhibits a descending trend. Comparing with the melting process, effects of increasing fin's height is more significant in solidification process.

Besides the shell-and-tube configuration, numerical investigation on plate-type LHS is also conducted by Gharebaghi and Sezai [38] for rectangular heat sink. Sharifi et al. [39] developed an analytic model to predict the melting period of PCMs. Mahmoud et al. [40] conducted different arrangements for heat sink with PCMs at different melting temperature. It is concluded that increasing fin number is good for heat distribution in LHS unit and leading to lower the peak temperature of heat sink. Arshad et al. [41] studied the effects of pin thickness as well as the volume fraction of PCMs on the cooling performance of heat sinks for electronic devices. The volume fraction of PCMs is kept at 9%. The heating boundary is assumed as uniform heat flux. Heat sinks are finned or not finned. The thickness of fins is ranging from 1 mm to 3 mm, with the interval of 1 mm. The volume fraction of PCMs is ranging from 0 to 1, with the interval of 0.33. Rahimi et al. [42] investigated with the charging and discharging processes of PCMs in finned-tube heat exchanger in experiments. The utilization of fins reduces the melting and solidification periods. It is also reported that the increase of inlet temperature is more effective for melting time reduction in the bare tube heat exchangers. The variation of flow rate of HTF is also more intensely influential on the solidification time for the bare tube heat exchangers.

As reported in the review paper contributed by Nasiru et al. [1], the presence of fins improve the heat transfer during the phase change process, regardless of the make-up and geometry of the LHTES systems. However, few studies considered the effects of fin numbers on thermal response of the LHS unit. Although the trend is easy to find, the quantitative analysis will help the optimal design in practice.

2.3.4. Using multi-PCMs

The increase of ΔT_m should be expressed more precisely as the uniform distribution of the temperature difference between PCMs and HTF in LHS unit, during charging and discharging process. The benefits can be not only evaluated with the energy basis, but also with the exergy/entropy basis as well as the entransy basis, which is proposed in the recent decade.

According to the demand of uniform temperature difference between PCMs and HTF, the melting temperature of PCMs should decrease alongside the flow direction of HTF in charging process and increase alongside the flow direction of HTF in discharging process. This is usually realized by the transverse of flow direction of HTF in two processes.

Fang and Chen [43] numerically investigated the effects of multiple PCMs on the performance of LHS unit. It is concluded that difference of melting temperature between multiple PCMs is crucial for performance improvement. Wang et al. [44] proposed a new concept of homogeneous phase change process using multiple PCMs to significantly decrease the melting/solidification periods. Cui et al. [45] numerically analyzed the structure with three types of PCMs for solar receiver. It is reported that the fluctuation of HTF outlet temperature is better controlled, comparing with single PCMs. More energy flowrate is also expected. Hu et al. [46] proposed a thermal storage system with frustum-shape. Along the flow direction of HTF, volume of PCMs change. Maximum five types of PCMs are adopted in the LHS unit. It is found effective even at small temperature difference. However, there is also some report about the asynchronous effects of multiple PCMs on the charging process and the discharging process, by Kurnia et al. [47]. It is concluded that the arrangement of PCMs with high melting temperature at the inlet of HTF would improve the heat transfer in discharging process, but may slightly worsen the charging process.

Thus, the major factor for multiple PCMs design is the match of melting temperature of PCMs in LHS unit. To better understand this issue and to provide guidance for the design of LHS unit, optimization of multi-stage LHS unit with multiple PCMs is conducted. Since there is no heat-and-work conversion during the operation of LHS unit, entransy theory is also adopted for optimization, besides the traditional energy and exergy/entropy analysis.

Tao et al. [48] reported the melting temperature match for double-stage LHS unit in charging process. Zhao et al. [49] reported the melting temperature match for multi-stage LHS unit in charging process. Wang et al. [50–52] reported the optimized match of melting temperature and surface for heat transfer of double- and multi-stage LHS unit in charging and cycle period.

However, less attention has been paid to the transient process optimization as well as other factors influencing the operation of LHS unit. Moreover, the comparison between entransy analysis and exergy analysis is important. Works are undergoing in our group. It is found that the difference between optimum melting temperature of nearby PCMs is constant in entransy analysis, while the ratio is constant in entropy analysis. The detailed discussion will be made. However, still the reason lies there, not so easy to answer, although we know that is superficially due to the difference between the optimization goals.

2.3.5. Encapsulation

Encapsulation of PCMs is also an effective method for heat transfer improvement in PCMs region. The mechanism may be explained as the reduce of heat transfer path as well as the increase of surface conducting heat transfer. Encapsulation of PCMs is to disperse PCMs in LHS unit into groups of small-sized particles closed and surrounded by other materials or the derivatives of PCMs itself after procedure of treatment. So, the direct property of PCMs is actually not changed, and the benefits are mainly contributed to the performance improvement of LHS unit as discussed later. The main research lies on the selection of raw-material and the method of encapsulation, as reviewed by Jacob and Bruno [53], Liu et al. [54], Saman et al. [55], Liu et al. [56], etc.

Jamekhorshid et al. [57] and Su et al. [58] reviewed the microencapsulation methods of PCMs. Milian et al. [59] reviewed on specific encapsulation techniques for inorganic phase change materials and the thermophysical properties. Sketch of encapsulated PCMs is expressed in **Figure 3**. The shell can be single layered or multiple layered or linked matrix, and the core can be single zone or several isolated zones. The shape could be regular, such as spherical, tubular or oval and irregular.

The methods of encapsulation are summarized in **Table 2**.

As far as the shell is concerned, Jacob and Bruno [53] reviewed on the shell materials in the encapsulation for high temperature thermal energy storage. Steel, nickel, sodium silicate,

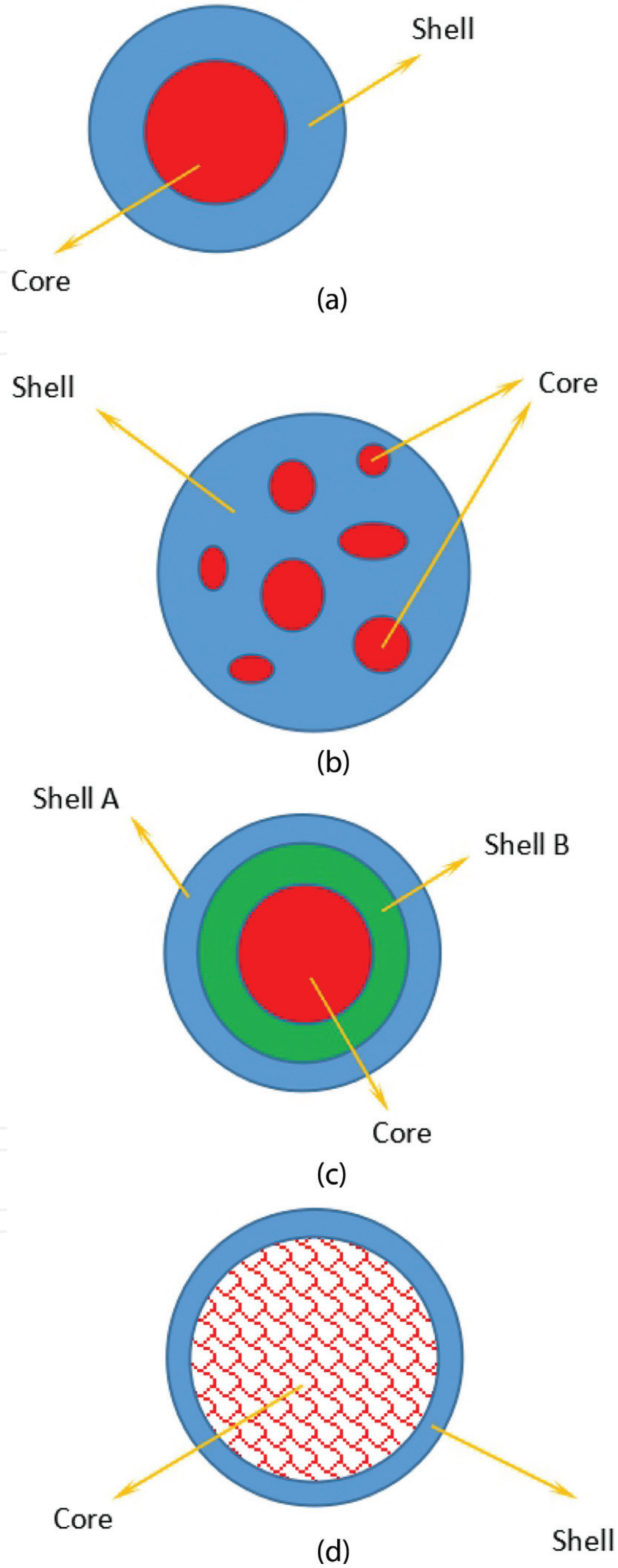

Figure 3. Sketch of encapsulated PCMs shapes. (a) Mononuclear; (b) polynuclear; (c) multi-wall; (d) matrix.

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Physical methods	Chemical methods	Physic-chemical methods
Pan coating	Interfacial polymerization	Ionic gelation
Air-suspension coating	Suspension polymerization	Coacervation
Centrifugal extrusion	Emulsion polymerization	Sol-gel
Vibration nozzle		
Spray drying		
Solvent evaporation		

Table 2. Methods of encapsulation of PCMs.

silicon dioxide, calcium carbonate and titanium dioxide are identified as shell materials. It is better to further consider the corrosion between shell materials and PCMs encapsulated, which is important for long-term stability as well as cost reduction. Ma et al. [60] reported an encapsulated metallic phase change materials. The shell material is iron and the core material is copper. The preparation is based on aerodynamic levitation method. It is concluded that the morphology evolution is attributed to the combined effects of liquid phase fraction of two not-miscible liquids, Stokes and Marangoni velocities of droplets, as well as the rotation direction of particles in the solidification process. Chen et al. [61] reported the preparation of nanocapsules. The core PCMs is n-dodecanol and the encapsulation method is miniemulsion polymerization with polymerizable emulsifier. The diameter is measured as 150 nm and the phase change temperature is 18.2°C. Yang et al. [62] proposed a hybrid elastomeric spherical structure. It is composed of foam core and solid shell. The performance is predicted with numerical investigation.

2.3.6. Application of heat pipe

Heat pipe is a thermal carrier to transfer heat from hot medium to cold medium spatially separated. Heat pipe has its own working fluid, flowing inside at closed or open mode. At the end of hot medium, the liquid phase working fluid evaporates and flows to the end of cold medium, where the gas phase working fluid condensates and flows back to the end of hot medium and makes a cycle. Since phase change is involved, heat pipe usually can supply better performance of heat transfer between hot medium and cold medium.

There are two operation modes of HP in LHS unit. The first is simultaneous heating for discharging and cooling for charging, and the other is intermittent heating and cooling. To some extent, the latter mode is easier to understand, and the former mode is better for the power match and good for continuous operation. In the intermittent mode, PCMs operates as the hot end of HP in discharging process of LHS unit and as the cold end of HP in charging process.

Shabgard et al. [63] developed a thermal network model to investigate the performance of cascaded PCMs and conducted exergy analysis. Shabgard et al. [64] considered the transient response of HP-assisted LHTES system with a 2D model. It is concluded that HP spacing is the key parameter for LHS unit design and controls the dynamic response of the system. Robak et al. [65] experimentally investigated the performance of HP-assisted LHTES system. It is concluded that with the assistance of HP, heat transfer during discharging process is almost twice improved. Bergman et al. [66] numerically investigated the performance of LHTES with HP in solar thermal power plant and reported increased charging/discharging rate of PCMs for two kinds of HTF flow pattern. Nithyanandam and Pitchumani [67] conducted a similar computational analysis on 3D physical model. In another work of Nithyanandam and Pitchumani [68], dynamic performance behavior of HP-assisted LHTES system is investigation with the consideration of cyclic operation.

However, most of the research is based on gravity-assisted HP. With the development of HP technology, other kinds of HP should also be considered for application in LHS unit. Moreover, it is found that most of the HP-assisted LHTES system is analyzed numerically and less attention has been paid to the experimental analysis. This will be an open field for research in the future.

2.3.7. Combined heat transfer enhancement techniques

With two or more techniques, such as the combination of fin-structure and heat pipe, or the combination of multiple PCMs and heat pipe, it is expected possible to further improve performance of LHS unit. Jung and Boo [69] numerically investigated the transient behavior of a LHS unit with fin-structured heat pipe. They used a row-by-row analysis method to estimate the layer necessary for system design. It is concluded that the increase of pitch would help increase heat transfer rate. Khalifa et al. [70] compared the performance of bare heat pipe and finned heat pipe. It is concluded that with fin-structure, energy efficiency is improved significantly. Nithyanandam and Pitchumani [71] conducted numerical analysis on LHSTES system with metal foam and embedded heat pipe. It is reported that the augmentation in heat transfer rate during charging decreased with pore-density of metal foam, due to the restriction in the formation of buoyancy-induced convection.

3. Numerical studies of PCMs

Although the results of numerical analysis are not always the case in practice, it offers an important way to investigate the process as well as the performance of phase change materials as well as latent heat storage units, characterized with less cost and short time occupation as well as convenience of parameter adjustment. The focus and the core in numerical analysis rely on the model used as well as the verification and modification of numerical models with experimental results.

3.1. Numerical models

Esen et al. [72] applied two models to describe the diurnal transient behavior of energy storage tanks. In the first model, HTF is flowing outside of pipe, the inside of which is filled with PCMs. In the second model, HTF is flowing inside of pipe, the outside of which is surrounded with PCMs. Two-dimensional analysis is conducted with enthalpy-based method, coupled with convective heat transfer between HTF and PCMs. The effects of properties of PCMs, parameters of geometry, such as the radius and height of cylinder or pipe, and characters of HTF, such as velocity and inlet temperature, on the melting time are discussed (**Figure 4**).

The expression of Nu is listed as:

For heat transfer inside tube:

$$Nu_p = 3.66(\text{Re} \leq 2200) \tag{4}$$

$$Nu_p = 0.023 \cdot \text{Re}^{0.8} \cdot \text{Pr}^{0.4}(\text{Re} > 2200) \tag{5}$$

For heat transfer outside tube:

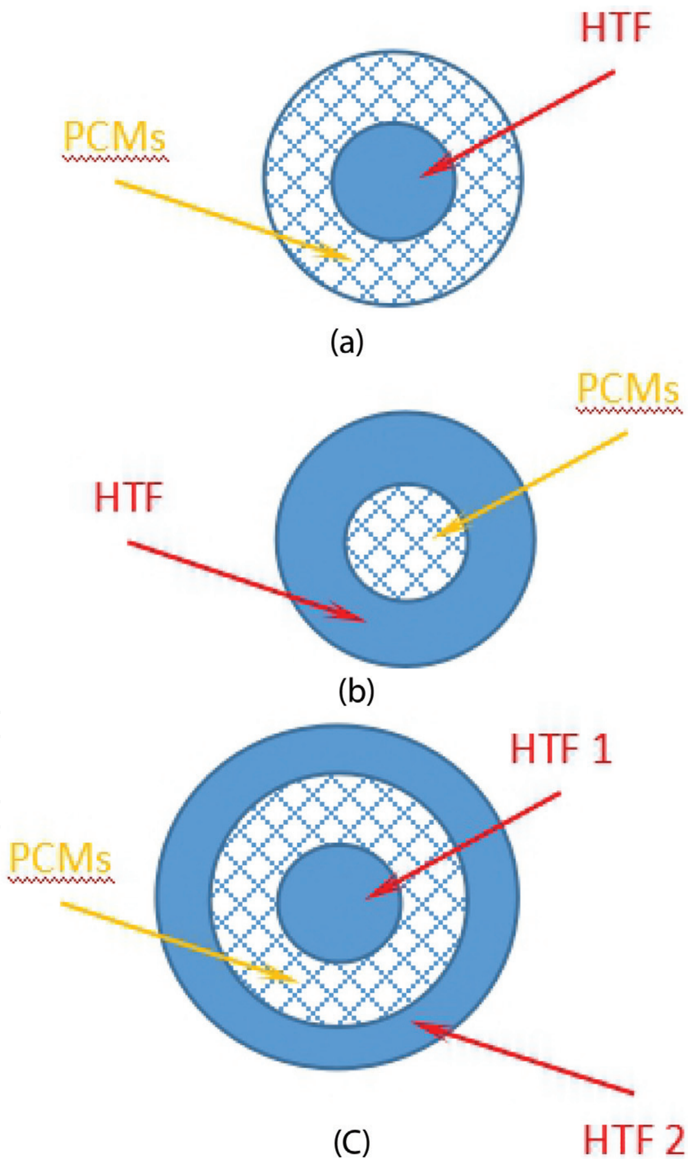

Figure 4. Configuration of HTF passage. (a) Outside of tube; (b) inside of tube; (c) annual between tubes.

$$Nu_c = 3.66 + 4.12 \cdot \left(\left(\frac{D}{R}\right) - 0.205\right)^{0.569} \text{Re} \leq 2200 \tag{6}$$

$$\frac{Nu_c}{Nu_p} = 1.08 - 0.794 \cdot e^{-1.62 \cdot \frac{D}{R}} \text{Re} > 2200 \tag{7}$$

Xia et al. [73] analyzed the heat transfer of latent thermal energy storage (LTES) system based on the effective packed bed model. The flow field is simplified as the flow through voids of a bed packed with PCMs particles. The random packing model is proposed for better simulation. The material properties and the thickness of encapsulation are two major factors for the heat transfer performance of a LTES bed.

The porosity is listed as:

$$\varepsilon_r = \varepsilon_\infty \cdot \left(1 + \left(\frac{0.87}{\varepsilon_\infty} - 1\right) \cdot e^{-5 \cdot \left(\frac{\frac{D}{2} - r}{d}\right)}\right) \tag{8}$$

$$\varepsilon_{3D} = \frac{n_{3D} \cdot \frac{4}{3} \cdot \pi \cdot \left(\frac{d}{2}\right)^3}{\pi \cdot \left(\frac{D}{2}\right)^2 \cdot H} \tag{9}$$

$$\varepsilon_{2D} = \frac{n_{2D} \cdot \pi \cdot \left(\frac{d}{2}\right)^3}{\pi \cdot \left(\frac{D}{2}\right)^2 \cdot H} \tag{10}$$

Izquierdo-Barrientos et al. [74] presented a dimensionless numerical model for the evolution of enthalpy with temperature, instead of constant phase change temperature assumption.

The dimensionless parameters include:

$$\widehat{T} = \frac{T - T_0}{T_{\max} - T_0} \tag{11}$$

$$\widehat{\theta} = \frac{\theta - T_0}{T_{\max} - T_0} \tag{12}$$

$$\widehat{\psi} = \frac{\psi - T_0}{T_{\max} - T_0} \tag{13}$$

$$\widehat{t} = t \cdot \frac{u}{H} \tag{14}$$

$$\widehat{x} = \frac{x}{H} \tag{15}$$

Modi and Perez-segarra [75] developed a one-dimensional numerical model for a single-tank thermocline thermal storage system in the concentrated solar power plant. The influence of types of heat transfer fluid, the temperature difference stored in HTF as well as the cycle cut-off on system performance is investigated. Two aspects are taken as criterion for comparison, that is, cyclic behavior of the system and the time required for equilibrium state attainment.

The heat transfer coefficient is expressed as:

$$h = \frac{6 \cdot (1-\varepsilon) \cdot k \cdot \left(2 + 1.1 \cdot \mathrm{Re}^{0.6} \cdot \mathrm{Pr}^{\frac{1}{3}}\right)}{D^2} \tag{16}$$

Opitz and Treffinger [76] developed a general heterogeneous model of heat transfer in packed beds. Lumped element formulation is implemented. The results are verified with two different experiments cited from references. No necessary to calibrate theoretical model with experiment results is reported.

The pressure drop for one layer of the packed bed is expressed as:

$$\Delta P = 150 \cdot \frac{(1-\varepsilon)^2}{\varepsilon^2} \cdot \frac{\eta}{d^2} \cdot w \cdot H + 1.75 \cdot \frac{(1-\varepsilon)}{\varepsilon^3} \cdot \frac{\rho}{d} \cdot w^2 \cdot H \tag{17}$$

The heat transfer is summarized as:

With correlation of Coutier and Farber:

$$h_{\mathrm{fs}} = \frac{700}{6 \cdot (1-\varepsilon)} \cdot \left(\frac{m}{A}\right)^{0.76} \cdot d^{0.24} \tag{18}$$

With correlation of Gnielinski:

$$Nu_{\mathrm{fs,\,i}} = f_{\mathrm{a}} \cdot \left(2 + \sqrt{(Nu_{\mathrm{lam,\,i}})^2 + (Nu_{\mathrm{turb,\,i}})^2}\right) \tag{19}$$

$$Nu_{\mathrm{lam,\,i}} = 0.644 \cdot \sqrt{\mathrm{Re}_{\mathrm{bed,\,i}}} \cdot \sqrt[3]{\mathrm{Pr}_{\mathrm{f,\,i}}} \tag{20}$$

$$Nu_{\mathrm{turb,\,i}} = \frac{0.037 \cdot (\mathrm{Re}_{\mathrm{bed,\,i}})^{0.8} \cdot \mathrm{Pr}_{\mathrm{f,\,i}}}{1 + 2.443 \cdot (\mathrm{Re}_{\mathrm{bed,\,i}})^{-0.1} \cdot \left((\mathrm{Pr}_{\mathrm{f,\,i}})^{\frac{2}{3}} - 1\right)} \tag{21}$$

$$f_{\mathrm{a}} = 1 + 1.5 \cdot (1-\varepsilon) \tag{22}$$

$$\frac{1}{h_{\mathrm{fs,\,p,\,i}}} = \frac{1 + \frac{Bi}{5}}{h_{\mathrm{fs,\,i}}} \tag{23}$$

$$Bi_{\mathrm{bed}} = h_{\mathrm{fs}} \cdot \frac{d_{\mathrm{p}}}{k_{\mathrm{bed}}} \tag{24}$$

Amin et al. [77] developed an effectiveness-NTU model of a thermal storage system with packed bed of encapsulated PCMs with the sphere shape. The two-dimensional representation is proposed to predict the heat transfer during phase change, comparing with one-dimensional phase change assumption in other configurations. A new definition of thermal resistance between HTF and PCMs is developed, taking the phase change process into consideration.

The heat transfer is expressed as:

$$Nu = \left(7 - 10 \cdot \xi + 5 \cdot \xi^2\right) \cdot \left(1 + 0.7 \cdot \mathrm{Re}^{0.2} \cdot \mathrm{Pr}^{\frac{1}{3}}\right) + \left(1.33 - 2.4 \cdot \xi + 1.2 \cdot \xi^2\right) \cdot \mathrm{Re}^{0.7} \cdot \mathrm{Pr}^{\frac{1}{3}} \quad (25)$$

Karthikeyan and Velraj [78] compared several mathematical models for numerical investigation of packed bed with encapsulated spherical PCMs. The enthalpy formulation technique is used to accommodate the phase change behavior of paraffin. Fully explicit finite difference method is adopted for solving numerical models. It is reported that the validity of model depends on the kind of HTF.

The governing equations are listed as:

For model 1:

$$\varepsilon \cdot \rho_{\mathrm{f}} \cdot A_{\mathrm{c}} \cdot L \cdot c_{\mathrm{f}} \cdot \left(\frac{\partial T_{\mathrm{f}}}{\partial t} + v_{\max} \cdot \frac{\partial T_{\mathrm{f}}}{\partial x}\right) = h_{\mathrm{s}} \cdot a_{\mathrm{p}} \cdot \left(T_{\mathrm{p}} - T_{\mathrm{f}}\right) \quad (26)$$

$$(1 - \varepsilon) \cdot \rho_{\mathrm{p}} \cdot A_{\mathrm{c}} \cdot L \cdot c_{\mathrm{p}} \cdot \left(\frac{\partial H_{\mathrm{p}}}{\partial t}\right) = h_{\mathrm{s}} \cdot a_{\mathrm{p}} \cdot \left(T_{\mathrm{f}} - T_{\mathrm{p}}\right) \quad (27)$$

For model 2:

$$\varepsilon \cdot \rho_{\mathrm{f}} \cdot A_{\mathrm{c}} \cdot L \cdot c_{\mathrm{f}} \cdot \left(\frac{\partial T_{\mathrm{f}}}{\partial t} + v_{\max} \cdot \frac{\partial T_{\mathrm{f}}}{\partial x}\right) = k_{\mathrm{f}} \cdot \frac{\partial^2 T_{\mathrm{f}}}{\partial x^2} + h_{\mathrm{s}} \cdot a_{\mathrm{p}} \cdot \left(T_{\mathrm{p}} - T_{\mathrm{f}}\right) \quad (28)$$

$$(1 - \varepsilon) \cdot \rho_{\mathrm{p}} \cdot A_{\mathrm{c}} \cdot L \cdot c_{\mathrm{p}} \cdot \left(\frac{\partial H_{\mathrm{p}}}{\partial t}\right) = k_{\mathrm{p}} \cdot \frac{\partial^2 T_{\mathrm{p}}}{\partial x^2} + h_{\mathrm{s}} \cdot a_{\mathrm{p}} \cdot \left(T_{\mathrm{f}} - T_{\mathrm{p}}\right) \quad (29)$$

For model 3:

$$\varepsilon \cdot \rho_{\mathrm{f}} \cdot A_{\mathrm{c}} \cdot L \cdot c_{\mathrm{f}} \cdot \left(\frac{\partial T_{\mathrm{f}}}{\partial t} + v_{\max} \cdot \frac{\partial T_{\mathrm{f}}}{\partial x}\right) = h_{\mathrm{s}} \cdot a_{\mathrm{p}} \cdot \left(T_{\mathrm{p}}\big|_{\mathrm{r=r_0}} - T_{\mathrm{f}}\right) \quad (30)$$

$$\rho_{\mathrm{p}} \cdot \left(\frac{\partial H_{\mathrm{p}}}{\partial t}\right) = k_{\mathrm{p}} \cdot \frac{\partial^2 T_{\mathrm{p}}}{\partial r^2} + \frac{2}{r} \cdot k_{\mathrm{p}} \cdot \frac{\partial T_{\mathrm{p}}}{\partial r} \quad (31)$$

3.2. Numerical simulation

Pakrouh et al. [79] present a numerical investigation on geometric optimization of heat sinks. Paraffin is selected as PCMs and aluminum is adopted as materials for heat sink and fins. The optimization parameters include the number of fins, the height of fins and the thickness of fins as well as the base. Natural convection is also taken into consideration. It reported a complex relation between PCMs and the volume percentage of thermal conductivity enhancers (TCEs). Shmueli et al. [80] investigated numerically with melting of PCMs in a vertical cylindrical tube and compared with experiments. The model is based on enthalpy-porosity formulation. The effects of parameters, such as the term describing the mushy zone in the momentum equation and the pressure-velocity coupling as well as pressure discretization schemes, are examined. No difference between PISO and SIMPLE schemes is found, while there is considerable difference between PRESTO and Body-Force-Weighted schemes. Local heat transfer and melting are compared and verified for numerical results. It is concluded that at the beginning of melting process, the heat transfer is mainly in the form of conduction in solid phase; while at the end of this process, the heat transfer is dominated by convection in liquid phase. Cascetta et al. [81] utilized FLUENT software to simulate the flow and heat transfer in an axisymmetric tank of cylindrical shape. Incompressible turbulent flow and fully developed forced convection is adopted in two-phase transient (LTNE-local thermal non-uniform) model to calculate the temperatures of fluid and solid phases. The porosity of filled bed is also considered variable in the radial direction and the thermal properties of both phases are related to temperature. The results agree well with experiments. Sciacovelli et al. [82] used enthalpy method to analyze the phase change phenomenon. Natural convection is neglected, due to the fully resolved fluid flow in the liquid phase. The evaluation of melting front as well as the temperature and velocity fields is studied in details. However, it is concluded that natural convection significantly affects the phase change process. Also in this paper, the effects of enhancement of thermal conductivity with the adoption of highly conductive nano-particles in PCMs are considered. Augment of thermal performance is found, due to the application of nano-particles. The melting time is reduced by 15% with 4% volume fraction of nano-particles. Similar results are also found for the heat transfer performance.

4. Conclusions

For the properties of PCMs under research, besides thermal conductivity and phase equilibrium, others such as supercooling [83], corrosion [84] and transportation [85] are also characterized and discussed. However, less attention has been paid on the systematic discussion. This is partly due to the diverse results in different research groups, and sometimes the conclusions are contradictory. For instance, Teng et al. [86] reported the advantage of multiwall carbon nanotubes (MWCNTs) over graphite for effective enhancement of thermal conductivity. However, Choi et al. [87] reported the contrary conclusion. Another case is the reported results of the same method and the same materials at different ages or by different groups are sometimes at significant variations. For instance, the heat of fusion for Paraffin Wax is reported as 173.6 kJ/kg [88] and 266 kJ/kg [89]; the melting temperature of myristic acid is reported as 49–51°C [90] and 58°C [91].

One of the reasons lies on the lackness of uniform standard or detailed information of preparation, manufacture and raw materials as well as the diversified methods of properties measurements. As far as thermal conductivity is concerned, researchers can utilize stationary and non-stationary methods to measure. Even in detailed non-stationary measurement, point-, linear- or surface- heating source is available for choice. Therefore, it seems difficult to collect the results in reference to obtain the regular of physical properties for theoretical estimation or analysis.

In this section, we mainly introduce the progress of property enhancement of PCMs and performance improvement of LHS unit. The detailed information of reported results is referred to cited references. It is found that lots of work has been done in the past decades and great progress has been made. However, there is still some weakness in research. For PCMs, most research is based on experimental measurement of properties, and less attention has been paid on the regular summary for theoretical estimation in the future or optimal design of composite material as well as energy storage unit. As far as LHS unit is concerned, it is the opposite condition, where most research is based on numerical analysis and less experimental research is conducted. This may lead to the deviation of the performance of LHS unit in application from the designed values, especially when the properties of PCMs as well as its composite are still not clear in details. What is more, the lackness of uniform standard and detailed report on information of preparation, manufacture and raw materials makes it difficult to collect the results of different groups and different ages all together.

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Conflict of interest

None declared.

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