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Effect of surface active agent on thermal properties of carbonate salt/carbon nanomaterial composite phase change material

Y.B. Tao *, C.H. Lin, Y.L. He

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

HIGHLIGHTS

- Nanomaterial aggregation weakens CPCM thermal performance.
- Larger nanomaterial specific surface area, worse CPCM thermal performance.
- SDS is a better SAA due to the less solid decomposition products.
- The 10 or higher mass ratio of SDS to nanomaterial is recommended.
- Thermal conductivity of CPCM can be enhanced 58.75%.

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ABSTRACT

Surface active agent (SAA) was used to improve nanomaterial dispersion during preparation process of carbonate salt/nanomaterial composite phase change material (CPCM) by solution evaporation method. In order to investigate the effects of SAA on CPCM thermal performance, three kinds of PCM samples were prepared and their thermal performances were characterized. The results show that nanomaterial dispersion greatly affects CPCM thermal performance. For CPCM without SAA, its thermal performance is weakened instead of enhanced due to nanomaterial aggregation and the weakening phenomenon is more obvious when nanomaterial has larger specific surface area. SAA decomposes during high temperature CPCM working process. And the effect of SAA on CPCM thermal performance has duality: on the positive side, SAA can improve nanomaterial dispersion and enhance CPCM thermal performance; on the negative side, SAA decomposition products may weaken CPCM thermal performance. So, SAA and its mass fraction should be carefully selected. Sodium dodecyl sulfate (SDS) is a better SAA for high temperature nano-CPCM and a high mass ratio of SDS to nanomaterial is recommended. With mass ratio of SAA to nanomaterial 10:1, PCM thermal conductivity can be enhanced up to 58.75% by adding 1 wt.% multi-walled carbon nanotubes.

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1. Introduction

The utilization of solar energy and industrial waste heat has attracted more and more attentions due to the globe energy crisis and environmental pollution. Thermal energy storage (TES) plays an important role in efficient utilization of solar energy and industrial waste heat, because it can solve the unstable and discontinuous problem of those energy sources and keep the energy utilization systems operating with high efficiency. Latent heat storage (LHS) with phase change material (PCM) as TES medium can provide better energy storage density and smaller temperature fluctuation [1]. LHS has been widely used in building energy saving [2], solar thermal utilization [3] and waste heat recovery [4] etc.

In the last decade, the effects of heat exchanger materials and patterns [5], PCM properties [6,7], geometric parameters [8,9], operating conditions [10,11] and liquid PCM natural convection [12] on LHS performance have been investigated. The research results provide valuable reference for practical application of LHS technologies. However, the thermal conductivities for most of PCMs are lower, which slows down thermal charging and discharging rates and restricts the large-scale application of LHS technology. So, investigations on performance enhancement method for LHS process are urgent to be carried out. Generally speaking, there are three kinds of enhancement methods: (1) enhance PCM thermal performance, for example using some high thermal conductivity additives to form CPCM [13–15], (2) adopt enhanced heat

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* Corresponding author. Tel.: +86 29 82664349; fax: +86 29 82665445.
E-mail address: yubingtao@mail.xjtu.edu.cn (Y.B. Tao).

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Nomenclature

c_p	specific heat ($Jg^{-1}K^{-1}$)
k	thermal conductivity ($Wm^{-1}K^{-1}$)
T	temperature (K)
T_m	melting point of PCM (K)
Δh	melting enthalpy (Jg^{-1})

Greek symbols

ω	mass fraction of nanomaterial

Subscripts

l	liquid
s	solid
PS	PCM/SAA composite

transfer surface, such as using enhanced heat transfer tubes[16–18], (3) enhance uniformity of heat transfer process, such as using multistage PCMs [19–21].

No matter which kind of enhancement methods is adopted, enhancing PCM thermal conductivity is always a direct and efficient way to improve LHS performance. Many kinds of nanomaterials have been adopted as additives to prepare nano-CPCM and improve PCM thermal conductivities. Cui et al. [14] experimentally studied the effects of carbon nanofiber and carbon nanotube additives on thermal behavior of soy wax and paraffin wax PCM. Li et al. [15] investigated the heat transfer enhancement effects for TES application using nanocomposite of stearic acid and multi-walled carbon nanotubes as PCM. Harikrishnan et al. [22] prepared a CPCM for building heating application with TiO_2, ZnO and CuO nanoparticles as additives and the solidification and melting characteristics of CPCM were investigated. Nurten et al. [23] adopted nanomagnetite to prepare paraffin-nanomagnetite composite to improve the thermal conductivity of paraffin. Warzoha et al. [24] experimentally investigated the effects of graphite nanofibers on thermal properties of organic paraffin PCM. Mehrali et al. [25] adopted graphene to enhance the thermal conductivity of palmitic acid PCM. Dheep and Sreekumar [13] reviewed the influence of nanomaterial on properties of latent heat solar thermal energy storage materials. However, most of the previous studies are focused on lower temperature PCM (such as paraffin waxes, fatty acids, polyalcohols and hydrated salts).

With the development of solar thermal power generation technologies, inorganic salts such as nitrates, chlorides, carbonates and their compositions have attracted more and more attentions to be used as high temperature PCMs. Huang et al. [26] prepared $LiNO_3$/KCl-expanded graphite composite PCM and experimentally investigated its thermal properties. Tao et al. [27] performed numerical studies on coupling heat transfer performance of solar dish collector with high temperature molten salts as PCM. The results show that non-uniform heat flux on LHS tube surface causes seriously non-uniform temperature distribution. Improving PCM thermal conductivity can make the temperature distribution more uniform, which is beneficial to both the system efficiency and life. In order to improve PCM thermal conductivity, Tao et al. [28] prepared carbonate salt/carbon nanomaterial CPCM with four kinds of carbon nanomaterials by solution evaporation method and the effects of nanomaterial microstructure and mass fraction on CPCM thermal performance were investigated.

The foregoing literature review shows that a lot of studies have been performed on the preparation and characterization of nano-CPCM. However, most of the previous studies are focused on lower temperature PCMs. And for the CPCM with nanomaterial as additive, the dispersion of nanomaterial in PCM has great effects on CPCM thermal performance. In order to improve nanomaterial dispersion, surface active agent (SAA) is usually adopted during CPCM preparation process. So, the actual nano-CPCM is a composite of nanomaterial, PCM and SAA. The interactions among them are very complicated, which results in the performance enhancement effects are different in different references. And for high temperature CPCM, SAA may decompose during the CPCM working process; the decomposition products will also affect CPCM performance.

In present paper, in order to investigate the effects of nanomaterial dispersion and SAA on thermal performance of high temperature carbonate salt/nanomaterial CPCM, three kinds of PCM samples were prepared. The thermal properties of the prepared PCM samples, such as specific heat, thermal conductivity, melting temperature and melting enthalpy were studied experimentally. Based on the experimental results, the effects of nanomaterial dispersion and SAA on CPCM thermal properties were concluded.

2. Experimental descriptions

Anhydrous lithium carbonate with purity ⩾97% and anhydrous potassium carbonate with purity ⩾99% are chosen to prepare binary carbonate eutectic salts (62 mol.%Li_2CO_3: 38 mol.%K_2CO_3), which is set as original PCM. The detailed thermal properties for the eutectic salts are shown in [28]. Four kinds of nanomaterials (single walled carbon nanotubes, SWCNT; multi-walled carbon nanotubes, MWCNT; graphene; fullerene C_{60}) are chosen as additives and used to prepare CPCM by solution evaporation method. Sodium dodecyl sulfate (SDS, $NaC_{12}H_{25}SO_4$) and sodium dodecyl benzene sulfonate (SDBS, $C_{18}H_{29}NaO_3S$) with purity ⩾99% are used as SAA to enhance the nanomaterial dispersion in CPCM.

Three kinds of PCM samples were prepared, including carbonate salts with nanomaterial only (PCM/nanomaterial composite), carbonate salts with SAA only (PCM/SAA composite), and carbonate salts with both nanomaterial and SAA (PCM/nanomaterial/SAA composite). The detailed preparation processes for the three kinds of PCM samples are concluded as follows.

(1) Put a certain amount of Li_2CO_3 and K_2CO_3 into a vacuum oven respectively and dry them for 3 h at temperature of 150 °C to remove moisture. Then weigh 232.95 mg Li_2CO_3 and 267.05 mg K_2CO_3 to prepare the binary carbonate eutectic salts (original PCM).
(2) Weigh nanomaterial (SWCNT, MWCNT, grapheme and fullerene C_{60}) with a certain mass ratio to the eutectic salts, such as 0.25%, 0.5%, 1.0%, 2.5%, 5% and 10% respectively.
(3) Weigh SDS and SDBS with a certain mass ratio to the eutectic salts, such as 1%, 5% and 10% respectively.
(4) Put the original PCM and weighed nanomaterial into sample vials with deionized water and ultrasonically vibrate them for 3 h to gain the PCM/nanomaterial solutions with different nanomaterial and its mass fractions. The solution samples for PCM/MWCNT with MWCNT mass fractions of 0.25%, 0.5%, 1.0% and 2.5% are shown in Fig. 1(a).

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