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Preparation and thermal properties characterization of carbonate salt/carbon nanomaterial composite phase change material

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ABSTRACT

To enhance the performance of high temperature salt phase change material, four kinds of carbon nanomaterials with different microstructures were mixed into binary carbonate eutectic salts to prepare carbonate salt/nanomaterial composite phase change material. The microstructures of the nanomaterial and composite phase change material were characterized by scanning electron microscope. The thermal properties such as melting point, melting enthalpy, specific heat, thermal conductivity and total thermal energy storage capacity were characterized. The results show that the nanomaterial microstructure has great effects on composite phase change material thermal properties. The sheet structure Graphene is the best additive to enhance specific heat, which could be enhanced up to 18.57%. The single walled carbon nanotube with columnar structure is the best additive to enhance thermal conductivity, which could be enhanced up to 56.98%. Melting point increases but melting enthalpy decreases with nanomaterial specific surface area increase. Although the additives decrease the melting enthalpy of composite phase change material, they also enhance the specific heat. As a combined result, the additives have little effects on thermal energy storage capacity. So, for phase change material performance enhancement, more emphasis should be placed on thermal conductivity enhancement and single walled carbon nanotube is the optimal nanomaterial additive.

1. Introduction

In recent years, the development of renewable energy and recovery of industrial waste heat have attracted more and more attentions due to the globe energy crisis and environmental pollution. The thermal energy storage (TES) plays an important role in the efficient utilization of renewable energy and industrial waste heat, because most of those energy sources are unstable and discontinuous. For example, the solar energy radiation density always changes with different weathers, times and seasons. So, high efficient TES materials and technologies are urgent to solve the present energy and environmental problems. Latent heat storage (LHS), which uses the phase change material (PCM) as the TES medium is considered as one of the most promising TES methods because it provides better energy storage density and smaller temperature fluctuation [1].

LHS has been widely used in building energy saving, electronic equipment thermal management, solar thermal utilization, and so on. A model compatible with solar assisted cylindrical energy storage tank and variation of stored energy with time for different phase-change materials was developed [2] and then the solar-aided cylindrical phase change storage tank was used for space heating [3]. An electronic equipment using carbon foam matrix saturated with phase change material and carbon nanotubes as thermal management modules was designed and the thermal characteristics were numerically investigated [4]. An indirect solar dryer using phase change material as energy storage medium was designed and experimentally investigated [5].

A lot of researches on the performance of LHS system have been performed. Esen et al. [6] performed geometric design of a solar-aided LHS system depending on various parameters and phase change materials. Sharma et al. [7] numerically investigated the effects of heat exchanger materials and patterns on performance of LHS system. Trp [8] performed experimental and numerical investigations of heat transfer performance during paraffin melting and solidification in a shell-and-tube LHS unit. Akgun et al. [9] experimentally studied the melting and solidification characteristics of paraffin as PCM in a tube in shell LHS system. Guo and Zhang [10] performed numerical simulation and parametric study on a new type of high temperature LHS system. Tao et al. [11] numerically investigated the effects of operating and geometric parameters on performance of high temperature molten salt LHS unit. Adine and Qarnia [12] numerically analyzed the thermal

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Nomenclature

c_p	specific heat, J g^{-1} K^{-1}	ΔH_m	enthalpy, J g^{-1}
k	thermal conductivity, Wm^{-1} K^{-1}		
q	TES capacity per unit CPCM, J g^{-1}	*Subscripts*	
T	temperature, K	e	final state
T_m	melting point t of PCM, K	eff	CPCM
		i	initial state
Greek symbols		l	liquid
α	thermal diffusivity, m^2 s^{-1}	s	solid
ω	mass fraction of nanomaterial	o	original PCM
ρ	density, kg m^{-3}		

behavior of a shell-and-tube LHS unit and the effects of heat transfer fluid (HTF) inlet temperature and mass flow rate on LHS performance were investigated. Tao and He [13] examined the LHS performance of PCM under non-steady-state HTF inlet boundary.

The aboved results provide valuable references for the practical applications of LHS technologies. However, the lower PCM thermal conductivity results in the lower thermal charging and discharging rates and restricts the large-scale application of LHS equipments. The performance enhancement for LHS process is urgent to be carried out. Generally speaking, there are three enhancement methods. (1) Enhance PCM thermal performance, for example adding some high thermal conductivity additives to form composite phase change material (CPCM). Cui et al. [14] performed the experimental exploration of carbon nanofiber and carbon nanotube additives on thermal behavior of PCM. Li et al. [15] investigated the heat transfer enhancement for thermal energy storage application using stearic acid nanocomposite with multi-walled carbon nanotubes. Harikrishnan et al. [16] 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. Dheep and Sreekumar [17] reviewed the influence of nanomaterials on properties of latent heat solar thermal energy storage materials. (2) Adopt enhanced heat transfer surface, such as enhanced heat transfer tubes. Seeniraj and Narasimhan [18] investigated the performance enhancement of a solar dynamic LHTS module having both fins and multiple PCMs. Mat et al. [19] studied the heat transfer enhancement for PCM melting in triplex tube with internal-external fins. Tao et al. [20] numerically investigated the performance of molten salt LHS system with finned tubes and different fin patterns were compared. (3) Enhance the uniformity of the heat transfer process, such as using multistage PCMs. Mosaffa et al. [21] presented the numerical investigations of performance enhancement of a free cooling system with a LHS unit employing multiple PCMs. Aldoss and Rahman [22] compared the performances of the single-PCM and multi-PCM thermal energy storage design. Tao et al. [23] performed optimization study on a two-stage latent heat storage unit based on entransy theory. No matter what kind of enhancement method is adopted, enhancing the PCM thermal conductivity is always a direct and efficient way to improve the LHS unit performance. A lot of researches have been performed for the preparation and characterization of CPCM to improve the thermal conductivities. However, most of the previous studies are focused on lower temperature PCM (such as organic PCM comprised of paraffin waxes, fatty acids and polyalcohols; together with some inorganic PCM like hydrated salts).

However, with the development of solar thermal utilization, especially solar thermal power generation technologies, researches on high temperature PCM and LHS equipments are becoming more and more urgent. Guo and Zhang [10] numerically studied the effects of geometry parameters and boundary conditions on the performance of a new type high temperature LHS system. Lu et al. [24] numerically investigated the filling dynamics of molten salt in cold receiver and the melting and solidification process were analyzed. Tao and He [25] performed three-dimensional numerical studies on LHS process of salt in a horizontal concentric tube to investigate the effects of liquid PCM natural convection on LHS performance. Tao et al. [26] numerically examined the coupling heat transfer performance of solar dish collector with high temperature salts as PCM and found the non-uniform heat flux on the tube surface resulted in non-uniform temperature distribution in PCM. The PCM thermal conductivity has great effects on temperature distribution. The larger PCM thermal conductivity will make the temperature distribution more uniform, which is beneficial to both the system efficiency and life. In those researches, the molten salts and molten salt compositions such as nitrates, chlorides, carbonates are chosen as the high temperature PCM. Kenisarin [27] reviewed the high-temperature PCM for thermal energy storage and most of the high-temperature PCM were molten salts or molten salt compositions.

In present paper, the emphasis was placed on the preparation and characterization of high temperature CPCM used for the solar power generation systems. The carbonate eutectic salts composition (62 mol.%Li_2CO_3:38 mol.%K_2CO_3) were chosen as the original PCM and four kinds of carbon nanomaterials (single walled carbon nanotubes, SWCNT; multi-walled carbon nanotubes, MWCNT; graphene; fullerene C60) are chosen as additives to prepare CPCMs and improve their thermal properties. Microstructures of the nanomaterial and prepared CPCM were characterized by scanning electron microscope (SEM). Thermal properties of the CPCM such as melting point, melting enthalpy and specific heat were investigated by differential scanning calorimetry (DSC). And thermal conductivity was measured by laser flash apparatus (LFA). Based on the experimental results, effects of nanomaterial microstructure and mass fraction on CPCM thermal properties were concluded.

2. Experimental descriptions

2.1. Materials

First of all, 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. Thermophysical properties for the carbonate eutectic salts were shown in Table 1, where the data of melting temperature and enthalpy are derived from [27] and the other data are derived from [28]. Then four kinds of nanomaterials (SWCNT, MWCNT, Graphene, C60) are chosen as additives and mixed into the original PCM to prepare CPCM. The real microstructures and geometric parameters for the four kinds