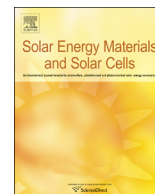




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Development of medium-temperature composite phase change material with high thermal stability and conductivity



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ABSTRACT

This paper reports firstly a medium-temperature ternary PCM of nitrate salt, containing 68 wt% KNO_3 , 18 wt% LiNO_3 , 14 wt% $\text{Ca}(\text{NO}_3)_2$ in weight. To improve its thermal stability under high temperature and long term conditions, CsNO_3 of quite low percentage (0–0.6 wt%) was attempted to add into the ternary nitrate salt to obtain quinary salts (KNO_3 - LiNO_3 - $\text{Ca}(\text{NO}_3)_2$ - CsNO_3). The thermal properties and stabilities of the nitrate salts without/with CsNO_3 were then carefully measured and analyzed. The results show that a low percentage of CsNO_3 does not influence the melting point of 113.0 °C, but reduces the fusion heat slightly by around 9.3%. The addition of CsNO_3 essentially improves the thermal stability of salts at high temperature of 400 °C for long duration and the thermal cycling stability under (100–180 °C) for 800 cycles. Two composites with 5 wt% and 10 wt% expanded graphite (EG) combined with the nitrate salt, remarkably raise the thermal conductivity of PCM by more than 20 times and 30 times, respectively. The increase of EG particle with extremely high thermal conductivity not only enlarges the specific surface area but tends to build interconnected structures in the composite, thus enhances the effective thermal conductivity of the composite. The novel PCM we developed here shows suitable thermal properties and good thermal stability in long term that make the composite PCM potential in improving the heat performance of latent heat storage system in medium-temperature applications.

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1. Introduction

Solar thermal energy, the largest natural energy source by far, will play an increasing role in meeting future energy needs [1–3], due to the energy shortage worldwide, continuous increases of greenhouse gas emissions and environmental pollutions. Discontinuity and instability are inherent characteristics of solar energy, how to improve the utilization efficiency is thus the key issue in developing solar thermal applications, particularly in medium- and high-temperature systems [4]. Koca et al. [5] gave a thorough discussion and summary on the design of solar thermal energy system (TES), and carefully analyzed the thermal and exergy efficiencies of different TES units integrated into power plant. Successful applications of solar energy rely, to a large extent, on an efficient and reliable thermal energy storage method.

Latent heat storage using phase change materials (PCMs) as working media is one of the most efficient methods to store thermal energy, based on the advantages of high storage density, isothermal nature during the phase change processes, heat recovery with small temperature drop, low vapor pressure at the

operational temperature, and chemical stability and non-corrosiveness [6–10]. A further advantage of latent heat storage is that heat storage and delivery normally occur over a fairly narrow temperature range which is the phase transition zone [11].

Solar thermal utilization can be classified into low- (< 80 °C), medium- (80–250 °C) and high-temperature (> 250 °C) applications [12]. Low-temperature solar thermal applications mainly include solar water heating which has been well developed and used worldwide. Most applications actually are in medium- and high-temperature regions such as solar drying, cooking, distillation and solar thermal power. According to the reference [13], 5–6% of the energy consumed annually in Germany is applied in temperature interval 100–300 °C. The developments of medium and high-temperature thermal storage utilizations, however, have obviously lagged behind.

Numerous chemical substances to this day can be used as PCMs, which are majorly classified as organic, inorganic, and eutectic [14]. To concise the introduction, only medium-temperature PCMs mostly relevant to our current work are concerned. Organic PCMs are available in a wide range of melting points [15], but fewer can be applied in medium-temperature systems by far. Sugar alcohols (SA) are considered as medium-temperature (90–200 °C) organic PCMs. Their melting points make them suitable for medium-temperature applications in solar process of heat or

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waste heat recovery. Compared to low-temperature SA, medium-temperature SA exhibited much larger degree of super cooling, consequently can curb the efficiency of thermal energy storage [16]. In addition, this kind of materials were found to undergo 10–15% volume expansion during melting [17] and poor stability [18]. Haillot et al. [19] analyzed the thermal storage behaviors of a series of PCMs in the range of 120–150 °C. Their results showed: dimethylpropionic acid (DMPA), maleic acid, and urea exhibited poor cycling stability; D-glucose indicated a low decomposition temperature; tris(hydroxymethyl)aminomethane (TAM) presented high transition sub-cooling; sebacic acid and polymeric hydrocarbons (HDPE) were detected to lose a small mass; adipic acid, benzoic acid, phthalic anhydride and dimethyl terephthalate can only be used in hermetically sealed crucibles.

Compared to organic PCMs, inorganic salt compositions used as PCMs are cheaper, more stable, and with higher thermal conductivity, but melt incongruently and are highly prone to phase separation and subcooling [14]. Kenisarin [20] summarized and discussed inorganic PCMs for storage thermal and a solar energy in the range of temperature 120–1000 °C, but most of the materials have melting point over 200 °C. Peng et al. [21] developed several nitrate mixtures composed of potassium nitrate, sodium nitrite, sodium nitrate with some additives, which can achieve a high temperature thermal stability (up to 550 °C) and a relatively low melting point 138 °C. In our previous work [22], we developed a class of inorganic nitrate salt compositions ($\text{KNO}_3\text{-Ca}(\text{NO}_3)_2\text{-LiNO}_3$) used for heat transfer fluid. The measured heat capacity curves showed that the mixtures have a significantly low melting point 80 °C, however accompanied by another obvious peak occurred at about 150 °C. This means that the compositions cannot form eutectic at 80 °C. Consequently, there may be an operational risk of freezing-up if the process temperature drops unexpectedly in a long term TES system. This potential instability of the compositions needs to be further quantitatively evaluated before applied in commercial applications. Raade et al. [23] developed a eutectic mixture of five alkali-nitrate salts, Halotechnics SS-500 (6 wt% NaNO_3 , 23 wt% KNO_3 , 8 wt% LiNO_3 , 44 wt% CsNO_3 , 19 wt% $\text{Ca}(\text{NO}_3)_2$), which has a low melting point 65 °C and thermal stability limit over 500 °C. The large addition of cesium nitrate reduces the melting point, but the cost of CsNO_3 is much higher than the other salts.

Moreover, the available PCMs have unacceptably low thermal conductivity ($\lambda=0.1\text{--}1.0\text{ W}/(\text{m K})$) [24], consequently slow down melting and solidification rates. A considerable techniques to overcome this limitation have been conducted to increase the heat transfer conductivity, either by adding the materials with high thermal conductivity such as metal matrix, carbon fibres or carbon fibre brushes, dispersing exfoliated graphite nano-platelets and expanded graphite (EG) to the PCM, or by generating macro/micro-encapsulation of PCMs. Our latest work [25] showed that the combination of organic PCMs with EG can form a stable composite, which is a simple and effective way to improve the thermal conductivities of PCMs by 41 times in maximum as well as prevents the liquid leakage during the solid-liquid phase change process. Other EG-based composites with organic PCMs, such as palmitic acid [26], n-octadecane [27] and acetamide [28] were developed, and the thermal conductivities of the composite PCMs with different weight fraction of organic substance were also measured. However, none of the EG-based composite PCMs is suitable for the medium- and high- temperature solar heat storage systems since their phase change temperatures are generally lower than 80 °C.

Motivated by Raade et al. work [23], this paper is directed towards the development of a new nitrate salt mixture with medium melting point and high thermal stability, through a little addition of CsNO_3 into the ternary nitrate salt ($\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2$). The thermal properties of the nitrate salts are experimentally

measured, focusing on melting temperature, fusion heat, high temperature thermal stability, and thermal cycle stability, together with the working temperature ranges of these mixtures. Furthermore, the nitrate salt/EG composite PCM is developed to improve the thermal conductivity of PCM.

2. Experiment

2.1. Materials preparation

2.1.1. Eutectic salt

A ternary eutectic salt based on $\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2$ was firstly prepared, named sample A. All component salts, KNO_3 , LiNO_3 and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). Since all salts have purities over 99%, no further purification process is required. A total of 110 g nitrate salts were weighed based on mole percent (Table 1) and mixed together. Loaded the mixture into a stainless steel container, then heated the container on a hot plate with temperature maintained at 200 °C to dissolve the component $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into liquid state. Dissolved water can absorb other salt components, and thus yields a homogeneous phase. The heating process lasted for 1 h to make sure the compound fully dehydrated.

The purpose of the above work is to design a ternary salt mixture with medium melting temperature around 110 °C, which is used as primarily component of PCM. To improve the thermal stability of the nitrate salt under high temperature (400–500 °C) for long term running, CsNO_3 purchased from SCRC with purity (> 99%) was attempted to mix into the ternary salt to obtain a quaternary salt $\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2\text{-CsNO}_3$. Totally, three quaternary salts (samples B, C, D) with increased weight percentages of CsNO_3 were prepared (Table 2). Their thermal properties including heat capacity and thermal conductivity, and thermal stabilities are to be measured.

2.1.2. Composite phase change material

Nitrate salts have quite low thermal conductivity (0.5 W/(m K)), which is a disadvantage for their applications in TES. To overcome this downside, EG with extremely high thermal conductivity was used to combine with nitrate salts to obtain composite PCMs. EG was prepared from expandable graphite powder to generate massive micropores with dimensions down to several microns. The expanded EG is worm-like structure (Fig. 1(a)), with a great number of micropores to create high specific area and large volume (Fig. 1(b)). The manufacture process has been detailedly given in our former work [25].

Two composites with 5 wt% EG and 10 wt% EG, respectively, were mixed with nitrate salt ($\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in terms of the scale in Table 1. Deionized water was used as solution to dissolve the eutectic salt to prepare unsaturated nitrate solution. Added EG into the nitrate solution, and blended the unsaturated solution by continuous stirring to promote the solution fully immersed into the micropores of EG and accelerate water evaporation as well. Put the mixture into an oven at 180 °C for 24 h, then the composite of ($\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2$)/EG in powder was obtained. Compared to Fig. 1(b), the micropores were well filled by the salts as evidenced from SEM pictures (Fig. 2(a) and (b)). Based on the Arrhenius equation [29], $\lambda = \sum_{i=1}^n x_i \lambda_i$ (where, λ ,

Table 1
Components of a ternary salt mixture sample A (unit: wt%).

Sample	KNO_3	LiNO_3	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
A	68.20	17.70	14.10

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