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Effect of nanoparticle dispersion on enhancing the specific heat capacity of quaternary nitrate for solar thermal energy storage application

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ABSTRACT

Molten salt is considered to be part of the main direction for studying high temperature heat transfer and storage medium in concentrated solar power due to its good thermo physical properties. Specific heat capacity performs a significant role in increasing the overall cycle efficiency and reducing the cost of heat transfer and storage. In this paper, in order to enhance the specific heat capacity, 1 wt% SiO_2 nanoparticles are added into a quaternary nitrate ($Ca(NO_3)_2$-KNO_3-$NaNO_3$-$LiNO_3$ with a low melting point called the low melting point salt (LMPS), which are mixed through ultra-sonication. Experimental results show that the specific heat capacity can be enhanced when nanoparticles are evenly distributed in the quaternary nitrate. The optimal ultra-sonication time with a frequency of 45 kHz is researched. The average specific heat capacity of nano-LMPS can reach up to 1.87 J/(g K) and the average enhancement reaches 19.4%. There is a good linear relationship between the specific heat capacity of nano-LMPS and ultra-sonication time. Scanning electron microgram images reveal that lamellar networks with higher density phase on the solid nano-LMPS surface exist and may cause the specific heat capacity enhancement of nano-LMPS.

1. Introduction

Concentrating solar power (CSP) system is one of the most promising ways to generate electricity and reduce global carbon dioxide emissions by using solar energy. By the end of 2013, the solar thermal power grid generation of the world has reached 3320 MW [1]. According to the report of the global current situation of renewable energy released by 21st century renewable energy network companies, the growth rate of new power stations reached 48% in 2014 as compared with 2012. From 2008 to 2013, the average growth rate has reached 35%, which is only second to the photovoltaic power and is far higher than that of wind power and other renewable energy power. To cope with the haze, the national plan on climate change (2014–2020), which was announced by the national development and reform commission of China, listed the use of wind power and solar power as key development areas, and listed the use of renewable energy as a key development direction. In 2015, the China state council agreed to set up the ZhangJiakou renewable energy demonstration area, and during the Olympic Games in ZhangJiakou, proposed to set up an internationally leading low carbon emission zone [2]. The DESERTEC solar thermal power project, associated with a group of 12 companies in Africa and Europe, aims to meet about 15% of the electricity demand in Europe by 2050 by building solar power plants in the desert of North Africa [3]. Hence, solar thermal power generation has been a key development direction all over the world.

Molten salts have been used in commercial solar thermal power plants as heat transfer fluid (HTF) and medium of thermal energy storage (TES) for its several apparent advantages, such as wide range of temperature use, low viscosity, low vapor pressure, good chemical stability, low cost, and environmental friendliness. For example, 1000 t molten salts have been used at the Archimedes power station (5 MW, Italy, 2010) to store heat for 8 h per day. Gemasolar power station (19.9 MW, Spain, 2011) used 8500 t molten salts to store heat for 15 h per day. The dosage of molten salts at the Andosol power station (50 MW, Spain) were as high as 2800 t for storing heat 7.5 h per day.

However, the specific heat capacity of molten salts is

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considered relatively low, which may result in the dramatic increase in the size of HTF/TES devices [4]. For instance, the specific heat capacity of $LiNO_3$ varies in the range of 1.670–1.845 J/(g K) at the temperature range of 300–400 °C and the average specific heat of Solar Salt (60 wt% $NaNO_3$+40 wt% KNO_3) and Hitec (53 wt% KNO_3+7 wt% $NaNO_3$+40 wt% $NaNO_2$) are 1.5 J/(g K) and 1.34 J/(g K), respectively [5,6]. Because of the low specific heat capacity, molten salts are in great demand in large-scale thermal storage systems, which greatly increases the investment and operation cost of solar power plants. In recent years, there have been many attempts to enhance specific heat capacity.

Nanofluids, first referred to by Choi et al. [7], were termed as solvent materials that contain nanoparticles. Compared with base fluids, the thermal conductivity of nanofluids enhanced anomalously. Numerous literatures have revealed similar enhancements of nanofluids with regard to effective thermal conductivity [8–11]. Similarly, some investigations of the specific heat capacity of nanofluids have been reported. Wang et al. [12] determined the specific heat capacity of nanoparticles by using mathematical models of statistical thermodynamics and revealed that the specific heat capacity increased when the particle size was decreased to the nanoscale. Bharath et al. [13] added SiO_2 nanoparticles with different sizes (i.e., 5, 10, 30, 60 nm) into solar salt and studied the laws of SiO_2 nanoparticles on enhancing the specific heat capacity of molten salt. Results showed an enhancement of 27% in the specific heat capacity of solar salt with added 60-nm SiO_2 nanoparticles. Ramaprasath et al. [14] studied the thermal laws of SiO_2 nanoparticles on enhancing the specific heat capacity of HitecXL by adding nanoparticles into HitecXL. Ho et al. [15] also showed an enhancement of 19.9% in the specific heat capacity of Hitec with added Al_2O_3 nanoparticles with an optimal concentration of 0.063%. Moreover, several studies had been done to investigate the enhancement of specific heat capacity by adding nanoparticles into the eutectic alkali chloride salts and eutectic of carbonate salts [16–18]. As previously noted, adding nanoparticles may be one of the key parameters for enhancing the specific heat capacity of molten salt.

However, there are two problems that must be addressed. (1) The melting point of the alternative molten salts is relatively high. For example, the melting point of solar salt is about 220 °C, about 142 °C for Hitec, and about 120 °C for HitecXL. Such condition could increase the operational risk of freezing and limit the application of molten salts in the CSP system. (2) Previous literatures all used ultra-sonication to disperse nanoparticles in nanofluids. As significant factors of ultra-sonication, the grade of frequency and time for sonication directly determine ultrasonic strength and nanoparticle dispersion. The ultrasonic waves can produce micro jet or cavitation bubbles with local high temperature and high pressure, which can significantly weaken the interaction energy between nanoparticles to prevent particles from agglomerating. When the grade of frequency is high, the cavitation bubbles rapidly form and break in the fluid, which work to disperse particles. However, such condition may also cause the small cavitation bubbles to reduce the sonication effect in dispersing nanoparticles. Moreover, continuously under ultra-sonication after dispersion, the nanoparticles can be sustained to absorb energy and consequently increase the interface energy that leads to the temperature enhancement around nanoparticles. As a result, the movement speed of nanoparticles is accelerated and the nanoparticles crash with each other more easily.

Therefore, in order to obtain even nanoparticle dispersion in nanofluids, appropriate frequency and time for sonication should be selected and studied. However, previous literatures did not report the impact of the ultra-sonication operating parameter on nanoparticle dispersion.

In order to decrease the melting point of molten salts, Ren et al. [19] experimentally developed a quaternary mixed nitrate (called low melting point salt (LMPS), KNO_3-$NaNO_3$-$LiNO_3$-$Ca(NO_3)_2\cdot 4H_2O$, 6:1:2:2 in mass ratio) by changing the compositions and doping new additives into solar salt. The melting point of the quaternary mixed nitrate has reduced to below 90 °C and the average specific heat capacity is about 1.54 J/(g K). Moreover, density, viscosity, thermal conductivity, and thermal stability have been researched. Experimental results confirmed that this quaternary mixed nitrate is suitable for applying to concentrated solar power plants.

In addition, the experimental results reported by Wang [20] show that there are significant heat capacity enhancements among nanostructured SiO_2. Therefore, the present study experimentally researches to improve the specific heat capacity of the LMPS by doping into SiO_2 nanoparticles and investigates the impact of ultra-sonication on nanoparticle dispersion. At present, the literatures about doping nanoparticles into the LMPS have never been reported.

2. Experiments

2.1. Nanomaterial synthesis

The procedures of preparing the LMPS with nanoparticles are as follows.

(1) The LMPS and SiO_2 nanoparticles are measured in proportions of 99 wt% and 1 wt%, respectively, by a high-precision balance (Mettle Toledo, ML204/02). The size of silica nanoparticles is 20 nm.
(2) The mixtures of LMPS and SiO_2 nanoparticles are dissolved in distilled water. The concentration of SiO_2 nanoparticles is around 0.1 g/L in the solution.
(3) The mixed solution is sonicated in an ultrasonic cleaner. The nanofluid is averagely divided into 8 portions and sonicated with a frequency of 45 kHz for multiple time buckets. The samples are listed in Table 1.
(4) Once the sonication processes are completed, the solutions are placed into a drying oven at 250 °C until the water completely evaporates. Finally, the nanomaterial LMPS samples are obtained.

2.2. Measurement of specific heat capacity

In the present investigation, the specific heat capacity is measured by using a differential scanning calorimeter (DSC, NETSCH, STA-449F3). By comparing the measurement results of the standard sample and the unknown sample, the Cp value of the unknown sample is calculated and the Cp value of the standard sample is known. Adopting sapphire (α-Al_2O_3) as the standard sample, the computational formula is indicated as [21]:

$$C_{p,s} = \frac{Hm_{st}}{hm_t} C_{p,st}$$

Table 1
Samples of nano-LMPS prepared by using ultra-sonication with frequency of 45 kHz for different time.

Number of samples	Time (min)	Frequency (kHz)
1	0	45
2	40	45
3	50	45
4	60	45
5	70	45
6	100	45
7	150	45
8	200	45