Enhanced Specific Heat Capacity of Molten Salt-Based Carbon Nanotubes Nanomaterials

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1 Introduction

Recently, depletion of fossil fuel and concern about global environment have led to promote and to intensify research into various renewable energy such as sunlight, geothermal, wind, tides, and so on. Among these renewable energy sources, solar thermal power generation systems have been considered as an attractive option to generate bulk power equivalent to conventional power plants. Currently, concentrating solar power (CSP) plants have been operated in several countries with various types of concentrating technologies [1].

Synthetic oil, pressurized steam, and molten salt eutectics are used as energy storage medium and heat transfer fluid in the CSP systems [2,3]. Although the synthetic oil such as Therminol is widely used in the CSP plants, its high vapor pressure restricts the operating temperature of the CSP power plants. While molten salt eutectics do not have the vapor pressure issue and make the CSP systems to be operable at higher temperature, their relatively poor thermal properties like specific heat capacity and thermal conductivity are impediment to improve the efficiency of the power plants and ultimately to reduce the generation cost of electricity. Therefore, enhancing thermal properties of the molten salt eutectics is important to improve the overall efficiency of the CSP power plants and to reduce the generation cost of the electricity [3].

With the development of nanoparticle synthesis technique, extensive studies into the nanofluids have been performed in the past decade. First of all, since anomalously increased thermal conductivity of nanofluids were reported in 2001, in which copper nanoparticles and CNTs were dispersed into ethylene glycol and into oil, respectively [4,5], an immense number of experimental studies about the thermal conductivity of nanofluids was performed with various nanoparticles [6–9]. Theoretical studies, as well as the experimental works, suggested several possible mechanisms to understand and to explain the enhanced thermal conductivity of nanofluids [10]. Additionally, research into the effect of nanoparticles on pool boiling characteristics and on the critical heat flux was also actively conducted under various experimental conditions [11–13]. While many people focused on the thermal conductivity and the boiling heat transfer of nanofluids, relatively a small number of studies was performed to measure specific heat capacity of the nanofluids. In 2008, Zhou and Ni reported that the specific heat capacity of water-based Al2O3 nanofluid was decreased with increase of the nanoparticle concentration [14]. Similarly, Vajjha and Das measured the specific heat capacity for three different water/ethylene glycol based nanofluids using nanoparticles of Al2O3, ZnO, and SiO2 [15]. They also obtained decreased specific heat capacity values compared with pure base fluids. Recently, Zhou and collaborators reported the similar results (decrease) for the specific heat capacity of ethylene glycol–CuO nanofluids [16]. While it was observed for the specific heat capacity to be decreased in several literatures, there were previous studies showing the enhanced specific heat capacity. In 2009, Nelson et al. measured the specific heat capacity of a polyalphaolefin (PAO) nanofluid with graphite nanoparticle fibers [17]. They measured a drastic enhancement of up to 50% by adding 0.6 wt.% of the nanoparticle in the PAO nanofluid. Shin and Banerjee observed the enhanced specific heat capacity by doping with silica nanoparticles in some molten salt eutectic such as the carbonate salt eutectic and chloride molten salt eutectic [18–20]. Bridges and collaborators [21] reported that the volumetric heat capacity of an ionic liquid was enhanced by doping with alumina nanoparticles by up to 45%. Most recently, Jo and Banerjee reported the enhanced specific heat capacity of molten salt nanomaterials in both liquid and solid phase [22,23]. They showed the effect of base materials [22] and dispersion homogeneity [23] on the specific heat capacity enhancement.

As introduced above, there is a controversy in the specific heat capacity of the nanofluids. According to the previous studies, it can be thought that the base materials and the nanoparticles affect...
the specific heat capacity of nanofluids (nanомaterials in liquid phase). Moreover, the effect of nanoparticle concentrations on the specific heat capacity enhancement such as a threshold concentration has not been sufficiently discussed for molten salt-based nanomaterials. This paper aims to measure the specific heat capacity of the carbonate salt eutectic-based CNTs nanomaterial using a DSC. The effect of nanoparticles (CNTs) concentrations on the specific heat capacity of the nanomaterial was examined for four concentrations. Three different temperature ranges were chosen to compare the specific heat capacity of the nanomaterials with that of the pure eutectic: in solid phase (250°C and 400°C) and in liquid phase (mean value between 525°C and 555°C). The SEM images were taken for both pre-DSC samples and post-DSC samples in order to confirm the CNT dispersion of the nanotubes into the carbonate salt eutectic and to find whether or not a remarkable change in the post-DSC samples was occurred during several thermal cycles in DSC. Finally, the comparison of the specific heat capacity between the experimental measurement in present study and theoretical predictions by conventionally used models was also discussed.

2 Materials and Methods

2.1 Nanomaterial Synthesis. A carbonate salts eutectic and multiwalled CNTs (CNT, Meliorum technologies, Rochester, NY) were used as a base material (solvent) and as nanoparticles, respectively. A surfactant, SDS (Sigma Aldrich, St. Louis, MO) was chosen to be a dispersant. The carbonate salt eutectic was composed of lithium carbonate (Li2CO3, 62 mol. %) and potassium carbonate (K2CO3, 38 mol. %), which were purchased from Sigma Aldrich. All chemicals were used as received in present study. The size of the CNT was 10–30 nm in diameter and 1.5 μm in length, according to the specification obtained from the manufacturer. Figure 1 shows a transmission electron microscopy (TEM, JEOL JSM-2010) image of CNT. As shown in the figure, the mean diameter of the nanotubes is quite similar to their specification. The concentration of CNT was varied from 0.1% to 5% in mass ratio.

Figure 2 shows the schematic of the procedures used to synthesize the carbonate molten salt eutectic-based CNT nanomaterials for specific heat capacity measurements. Initially, the CNT was dispersed in distilled water with the SDS (at a mass concentration of 1%) with respect to the eutectic to avoid agglomeration of the CNT. Then the colloid was subject to sonication in an ultrasonic bath for 2 hr. The aqueous salt solution was mixed with additional volumes of water and the aqueous CNT nanofluid. Then the suspension was sonicated again for 3 hr. Immediately after the sonication process, the water was evaporated using a syringe pump to obtain dry nanomaterial samples for the specific heat capacity measurements in DSC. The suspension was dispersed drop-by-drop on a beaker placed on a hot-plate at 250°C. Since SDS is easily decomposed by prolonged heating at a certain temperature over 40°C [24], and moreover it was obtained that fast water evaporation favorably affects the enhancement of the specific heat capacity in our previous study [23]. Hence, this syringe method was employed to minimize the water evaporation time, to avoid agglomeration of the CNT, and finally to augment the enhancement of the specific heat capacity of the nanomaterials. In order to confirm whether the nanotubes were well mixed with the salt eutectic, TEM (JEOL JEM-2010) images were taken for pre-DSC samples as show in Fig. 3. From this image, it can be observed that the salt eutectic mixed homogeneously with the CNTs. In addition, SEM (JEOL JSM-7500F) for pre-DSC samples and post-DSC samples was also taken to examine differences in the CNT dispersion after the thermal cycles in DSC.

2.2 Specific Heat Measurements. The specific heat capacity values of the nanomaterials and pure eutectic were measured using DSC (TA instrument, model: Q20) for both solid and liquid states. Based on the measured difference in heat flow, the specific heat capacity was determined by following a standard protocol.
established by the American standard test method (ASTM E1269) [25]. According to this protocol, the difference in heat flow values between an empty pan (Tzero aluminum hermetic pans, TA instruments) and a reference material (a sapphire disk) was recorded as a function of temperature from the DSC instrument. The measurements were repeated using the same thermocycling protocol multiple times in every test for the individual samples (pure eutectic or nanomaterials). The temperature range was varied from 150°C up to 560°C. A ramp rate of 20°C/min was employed in the heating process. An isotermal process was used at the beginning and at the end of each thermal cycle (i.e., at 150°C and 560°C). The heat flow data of the first thermal cycle in the DSC were discarded in calculation of the specific heat capacity because the first heat flow curve was often observed to be skewed, probably due to thermal nonequilibrium issues. For the DSC test runs of the empty pans and the sapphire standard, the heat flow measurements from the first run were also discarded. After the first cycle, the measurements in DSC were repeated five times in order to ensure reproducibility of the experimental results and to verify if significant variation occurred in the measurements. The specific heat capacity values were compared in both solid and liquid phase: at 250°C and at 400°C for solid phase and mean values between 525°C and 555°C for liquid phase. Prior to the measurement of the specific heat capacity of nanomaterials, the specific heat capacity of pure eutectic was measured to compare with a reference value from a literature [26] in order to verify the experimental conditions and the materials themselves. The results for the nanomaterials were compared with that of the pure eutectic to examine the enhancements.

A theoretical model (thermal equilibrium model) shown in Eq. (1) which is based on the mass fraction of nanoparticles added was proposed to calculate the specific heat capacity of mixtures [27], and it has been used to validate the experimental results for the specific heat capacity of several nanofluids in previous literatures [14,16,28]. This theoretical model was employed in this study to predict the specific heat capacity of salt nanomaterials and to compare them with the experimental results

\[
c_{p,nf} = m_n \cdot c_{p,n} + m_f \cdot c_{p,f} - m_n \cdot c_{p,nf} \cdot m_f
\]

where \(m\) is the mass fraction, \(c_p\) is the specific heat capacity, subscript \(n\) indicates the nanoparticle, subscript \(nf\) indicates nanofluids, and subscript \(f\) indicates the base fluid (solvent).

### 2.3 Measurement Uncertainty

As mentioned above, the specific heat capacity was determined by ASTM method according to the following equation:

\[
c_{p,s} = c_{p,n} \frac{\Delta q_{st} \cdot m_a}{\Delta q_{st} \cdot m_s}
\]

where \(c_p\) is the specific heat, \(\Delta q\) is the heat flow difference between the specimen and the empty pan, and \(m\) is the mass. Subscripts, \(s\) and \(st\), indicate the samples (pure salt eutectic or nanomaterials) and the standard materials (sapphire in this study), respectively. The heat flow differences were obtained by subtracting baseline (empty pan, subscript \(b\)) heat flow from the heat flow of the sapphire and the sample. The measurement uncertainty is represented as follows [29]:

\[
U_{c_s} = \sqrt{\left(U_{(c_s)} \cdot \frac{c_s}{c_a} \right)^2 + \left(U_{(\Delta q)} \cdot \frac{\Delta q}{\delta (q)} \right)^2 + \left(U_{(\Delta q)} \cdot \frac{\Delta q}{\delta (q)} \right)^2 + \left(U_{(\Delta q)} \cdot \frac{\Delta q}{\delta (q)} \right)^2 + \left(U_{(m)} \cdot \frac{m}{m_a} \right)^2 + \left(U_{(m)} \cdot \frac{m}{m_s} \right)^2}
\]

The uncertainty was resulted from curve fitting of the specific heat capacity of the sapphire, the heat flow of the sample and the sapphire, and the mass of the sample and the sapphire. The uncertainties of the curve fitted specific heat capacity of the sapphire and the heat flow are ±0.3% and ±2%, respectively. The maximum measurement uncertainty in the determination of the specific heat capacity is estimated to be ±3.5%.

### 3 Results

#### 3.1 Specific Heat Capacity of Nanocomposites (Nanomaterial in Solid Phase)

Figure 4 shows the heat flow curves of a pure salt eutectic and a nanomaterial sample (containing CNTs of 5 wt.%). Comparing the two curves, it is observed that there is only a marginal difference in the magnitude of the heat flow curves for the two samples. It should be noted that the magnitude of heat flow curves depends on the amount of samples loaded in the test pan. Accordingly, it can be presumed no chemical reaction occurred between the salt eutectic and the CNT (including SDS) over the whole temperature range in which measurements were performed.

The specific heat capacity of the nanocomposites and the enhancement at 250°C for four different concentrations of CNT are shown in Fig. 5. A simple correlation for the specific heat capacity of the pure carbonate salt eutectic at a certain temperature range suggested by Araki et al., was presented in the following equation [26]:

\[
c_p = 0.562 + 1.16 \times 10^{-3} \cdot T (J/gK) \quad (365 \leq T \leq 631K)
\]

where \(T\) indicated the absolute temperature. At 250°C, the literature value is 1.169 (J/gK), and similarly the experimental value obtained in our previous study was 1.19 (J/g K), which is a marginally different from the literature data but it is in reasonable agreement [30]. Compared with the specific heat capacity of the pure eutectic (1.19 (J/g K)), the measured specific heat capacity for the various concentrations of CNT was observed to be enhanced. As shown in Fig. 5, the specific heat capacity at the lowest concentration of CNT explored in this study (0.1 wt.%) was 1.24 (J/g K), which corresponds to the enhancement of about 4.0%. Taking the measurement uncertainty into consideration, the enhancement at

![Fig. 4 Heat flow curves of a pure eutectic sample and a nanomaterial sample obtained from DSC](image-url)
0.1 wt.% is within the margins of the measurement uncertainty (~3%). As the concentration of CNT was increased to 5%, the specific heat capacity was also increased up to 12.3%.

A similar behavior in the specific heat capacity of the nanocomposites was obtained at 250°C and 400°C as shown in Fig. 6. Figure 6 shows the specific heat capacity of the nanocomposites and the corresponding enhancements at 400°C. At the CNT concentration of 0.1 wt.%, almost the same specific heat capacity as that of the pure eutectic was obtained. At higher concentration of CNT, larger enhancement in the specific heat capacity values was observed. The highest enhancement obtained at 5 wt.% of CNT was 12.0% (which is similar to 12.3% at 250°C).

3.2 Specific Heat Capacity of Nanofluids (Nanomaterials in Liquid Phase). The specific heat capacity of the nanofluid samples (in liquid phase) was also measured in present study. In the literature, Araki and collaborators experimentally measured the heat capacity of the pure carbonate salt eutectic and they reported a constant value of 1.6 (J/g K) [26]. The specific heat capacity measured in this study was 1.612 (J/g K), and it was utilized to calculate the enhancements in the specific heat capacity for nanofluids [30]. Figure 7 shows the results for the enhancements of the specific heat capacity in liquid phase. The concentration dependence of the specific heat capacity of nanofluids was significant. The specific heat capacity results were significantly enhanced with increasing concentration of CNT. The most remarkable feature in the liquid phase was the relatively larger enhancements than those at both 250°C and 400°C (solid phase). In liquid phase, the specific heat capacity of the nanomaterial was significantly increased by up to 14.7% on mixing with CNT at mass concentration at 5%.

3.3 Theoretical Prediction of Specific Heat. Using the thermal equilibrium model in Eq. (1), the specific heat capacity of the nanofluids (nanomaterial samples in the liquid phase) was predicted as a function of the nanoparticle concentration. The specific heat capacity values of the eutectic, the graphite, and the CNT at three different temperatures are listed in Table 1. The specific heat capacity for the nanoparticles (CNT) which is needed to theoretically estimate the specific heat capacity of the nanofluid was obtained from a graphite value [31]. The theoretical predictions for the specific heat capacity values were plotted as a function of the temperature and the concentration of CNT in Fig. 8(a). As expected, larger enhancements in the specific heat capacity of the nanofluids with increasing amounts of CNT were observed. However, the theoretical predictions did not match the experimental data. As shown in Fig. 8(a), the maximum enhancement predicted by the thermal equilibrium model was less than 1% even at the CNT concentration of 5 wt.%. However, the enhancement in the experiments was obtained to be more than 14% at the same concentration of the CNT. The prediction from the thermal equilibrium model did not match the experimental results, even when the specific heat capacity of CNT (generally referred to as \(c_v\)) was replaced with the higher value for single walled CNTs network [32]. The maximum prediction value in Fig. 8(b) was about 2.5%, but it is still much less than the experimental results (12.3%).

4 Discussion

The lack of agreement between predictions from the theoretical model and the experimental data can be explained to be due to several factors. First, the specific heat capacity of the nanoparticle (CNTs in this study) is likely to be drastically increased.
Wang et al. calculated the specific heat capacity of a nanoparticle and also investigated the effect of the particle size and the temperature [33]. In their paper, they showed that the specific heat capacity can be enhanced with decrease in the size of the nanoparticle and with increase in temperature. Nelson et al. pointed out this effect as a possible reason for the enhanced specific heat capacity of the PAO-graphite nanofluids [17]. However, the specific heat capacity of the CNTs needs to be up to 350% at the temperature where the eutectic exists in liquid, for the theoretical model to match the experimental results. Therefore, although the enhanced specific heat capacity of the nanoparticles might be a significant contributor, it does not account for the observed enhancements for the specific heat capacity of the nanofluids.

As a unique feature of nanofluids, it was reported that a dense layer of liquid molecules (compressed liquid layer) is formed on the surface of the nanoparticles in experimental and computational studies. Oh et al. reported the evidence for ordering of liquid atoms adjacent to crystalline interface [34]. Molecular dynamics simulations, as well as the experimental proof by Oh et al., showed the formation of a compressed layer with a certain thickness at the interface between a solid nanoparticle and liquid molecules, for instance in the molten salt eutectic–CNTs nanofluids [22] and in the water–CNTs nanofluids [35]. This more ordered liquid regions which can be regarded to acquire a quasicrystalline structure can amplify the capability of thermal energy storage in the nanofluid. Hence, the specific heat capacity of the nanofluid can be modified by doping with a minute concentration of the nanoparticles in the salt eutectic samples. The compressed region of the liquid molecules is expected to play a significant role for the enhancements of the specific heat capacity of the nanofluids.

Wang et al. reported that the specific heat capacity of a solid phase, the increase in the specific heat capacity of the nanotubes themselves with temperature might play a more dominant role in raising the specific heat capacity. Relatively small enhancements of the specific heat capacity in solid phases can support this particular hypothesis.

Table 1 Specific heat capacity of pure carbonate salt eutectic, graphite, and CNTs

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Carbonate eutectic (J/g K)</th>
<th>Graphite [28] (J/g K)</th>
<th>CNT network [29] (J/g K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1.188</td>
<td>1.25</td>
<td>1.79</td>
</tr>
<tr>
<td>400</td>
<td>1.287</td>
<td>1.50</td>
<td>1.88</td>
</tr>
<tr>
<td>525–555 (liquid phase)</td>
<td>1.612</td>
<td>1.66</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Oh et al. showed the formation of a compressed layer with a certain thickness at the interface between a solid nanoparticle and liquid molecules, for instance in the molten salt eutectic–CNTs nanofluids [22] and in the water–CNTs nanofluids [35]. This more ordered liquid regions which can be regarded to acquire a quasicrystalline structure can amplify the capability of thermal energy storage in the nanofluid. Hence, the specific heat capacity of the nanofluid can be modified by doping with a minute concentration of the nanoparticles in the salt eutectic samples. The compressed region of the liquid molecules is expected to play a significant role for the enhancements of the specific heat capacity of the nanofluids. For the specific heat capacity enhancements in solid phase, the increase in the specific heat capacity of the nanotubes themselves with temperature might play a more dominant role in raising the specific heat capacity. Relatively small enhancements of the specific heat capacity in solid phases can support this particular hypothesis.
by dispersing nanoparticles. Additionally, percolated tube structures were also suggested as a significant factor for the drastically enhanced thermal conductivity of nanofluids [39]. This percolating network may also increase the thermal conductivity of the molten salt eutectic-based CNT nanomaterials, because these chainlike structures can enhance heat transport in the nanomaterials. However, it is presumed that the percolated CNTs do not play an important role in the enhanced specific heat capacity of the nanomaterials. As mentioned above, the effect of the compressed layers was much more dominant on the specific heat capacity of the nanomaterials. Thus, the percolating network structures can reduce the total volume of the compressed liquid layer due to increase of the effective nanoparticle size.

As shown in Figs. 5–7, the specific heat capacity of the nanomaterials was proportional to the concentration of CNT. The peak point where the specific heat capacity has the maximum value was not obtained in present study. Based on our speculation that the compressed liquid layer adjacent to nanoparticles increases the specific heat capacity of the nanomaterials, the agglomeration of CNT unfavorably affects the specific heat capacity enhancement, and the agglomerated CNT should increase with the CNT concentrations. Therefore, the specific heat capacity of the nanomaterials would have the maximum value at a certain concentration, and it could decrease with increase of the CNT concentrations.

In the present study, the specific heat capacity of the carbonate salt eutectic was enhanced by doping them with CNT, and the level of enhancement was much higher than the theoretical predictions. Since the thermal equilibrium model for determining the specific heat capacity of mixtures is a function of the specific heat capacity and mass fractions of the constituents, variations in the specific heat capacity of the nanofluids are entirely dependent on the amount of nanoparticles and their properties. Thus, the additions of CNT at small amounts concentration cannot enable the level of the specific heat capacity enhancement to be significant. Hence, there is a contradiction between the experimental results and the theoretical predictions. Although the theoretical model was in good agreement with the data for the specific heat capacity of aqueous nanofluids [14], this study reported degradation in the specific heat capacity of the aqueous nanofluids. Consequently, it is expected that the theoretical model may be applicable to limited cases such as liquid–liquid mixtures or liquid–vapor mixtures. Therefore, a new theoretical model which can be applicable for all nanofluids is needed.

5 Conclusions

The specific heat capacity enhancements for the carbonate salt eutectic-based CNT nanomaterial were observed for both solid and liquid phase. The effect of the CNT concentrations was investigated in this study. In addition, the experimental results were compared with the theoretical predictions. The knowledge gained from these experiments is summarized as follows:

(a) The specific heat capacity was significantly enhanced by up to about 15% in liquid phase by dispersing multiwalled CNTs at 5% mass concentration in the carbonate salt eutectic. Also, even at a minute concentration of CNT (0.1 wt. %), the specific heat capacity was enhanced in liquid phase. Moreover, in solid phase, the specific heat capacity enhancement was up to ~12% for the nanofluid with CNT at 5 wt.%.

(b) The specific heat capacity of the nanomaterial was gradually increased with the concentration of CNT. The enhancement was higher in liquid phase than in solid phase. This implies that a possible transport mechanism exists exclusively in liquid phase.

(c) The CNT dispersion was confirmed by TEM images for pre-DSC samples. In addition, no significant difference in SEM images between the pre-DSC samples and the post-DSC samples was observed.

(d) Theoretical prediction for the specific heat capacity values was obtained using a conventional analytical model. However, the prediction from the theoretical model did not...
match the enhancement for the specific heat capacity values, as observed in the experimental measurements. This shows that the literature model (which is based on mixing properties of immiscible substances or phases) is limited in applicability. Better theoretical models are required to estimate the specific heat capacity of the nanomaterials.

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Nomenclature

- \( c_p \) = specific heat capacity (\( \Omega/g \) K)
- \( m \) = mass (g)
- \( T \) = temperature (K or °C)
- \( \Delta q \) = heat flow difference (mW)

Subscripts

- \( b \) = baseline (empty pan)
- \( f \) = base fluid (base material)
- \( n \) = nanoparticle
- \( nf \) = nanofluid
- \( s \) = sample
- \( st \) = standard material

References