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Thermal characterisation of binary sodium/lithium nitrate salts for latent heat storage at medium temperatures

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A B S T R A C T

Latent heat storage in molten salt mixtures has been considered as a promising method for medium temperature solar thermal storage and industrial waste heat storage. The binary sodium/lithium nitrate salt mixture is one of the potential candidate materials. However there is limited information on their thermal performance except for their phase diagrams. In this paper, two binary salts, NaNO3–LiNO3 (46–54%) and NaNO3–LiNO3 (40–60%), were investigated to assess their suitability for medium temperature heat storage. The thermal properties and long term stability under multiple cycles of each binary salt pair were investigated using Differential Scanning Calorimetry (DSC). The chemical stability at elevated temperatures was tested using a Thermogravimetric Analyser (TGA). Both binary salts analysed have suitable melting temperatures (just under 200 °C) with relatively high latent heat values (>220 kJ/kg), both exhibiting good thermal and chemical stability.

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1. Introduction

Thermal energy storage, including sensible heat and latent heat storage, plays a key role in solar thermal energy and industrial waste heat storage. It has been considered as one of the most promising technologies for improving the effective use of available sources of heat when time of generation and demand do not match. Latent heat storage using PCMs has a bigger potential compared to sensible heat storage for some applications due to its high heat storage density within a narrow temperature range. According to the temperature, the latent heat storage can be divided into three groups: low temperature heat storage (<120 °C), medium temperature heat storage (120–300 °C) and high temperature heat storage (>300 °C). Many researchers have provided comprehensive reviews of the use of PCMs in solar thermal energy applications for the low temperature and high temperature heat storage. [1–7]. Most of the researchers, however, have not focused on the medium temperature range.

In the applications of solar thermal energy and industrial waste heat storage, PCMs with a melting temperature between 120 °C and 300 °C are also of great interest. For example, a large amount of heat in this temperature range is required to generate process steam for applications in food processing, production of paper and in the textile industry. Investigations into the thermal performance of molten salts in this temperature range have been carried out by researchers, mostly focused on developing salt mixtures with a low melting temperature that could be used as Heat Transfer Fluids (HTF), such as the Solar Salt (KNO3 40%–NaNO3 60%) and the Hitec Salt (KNO3 53%–NaNO3 7%–Na2O 40%) [8–10] (All the percentages in this paper are based on mole percentages). A desirable HTF should have a low melting temperature and low viscosity, whilst, in a latent heat storage system, the molten salts must have a suitable melting temperature (not as low may be better depending on the application temperature) and relatively high latent heat capacity. In addition, other properties such as thermal stability under repeated cycling, chemical stability, thermal expansion, compatibility with other heat storage system materials are also important. Lopez et al. [11,12] tested the thermal properties of a eutectic system of KNO3–NaNO3 (54–46%) with a reported melting temperature of 223 °C and a latent heat capacity of 106 kJ/kg. They pointed out that the eutectic system has desirable characteristics such as good chemical stability, no phase segregation, low corrosion and low cost. However, for use as latent heat storage, the latent heat of the eutectics is low. Huang et al. [13] studied a eutectic system of LiNO3–KCl and produced a heat storage medium with a relatively high latent heat of 178.10 kJ/kg. A Ca(NO3)2–NaNO3 mixture was tested by Zhao et al. [14] to determine its potential for latent heat storage applications. They concluded that a mixture of Ca(NO3)2–NaNO3 with a mole ratio of 3:7 demonstrated the best heat storage properties. In terms of latent heat, this was however low being less than 150 kJ/kg.

The nitrate/chloride mixtures are predominantly applied to be
heat storage media for their low melting temperature, high latent heat, high thermal stability, low unit cost and negligible vapour pressure. The potential nitrate/nitrite and chloride salt mixtures with their melting temperatures and latent heats are listed in Fig. 1. The molten salts with LiNO₃ have relatively high latent heats. However, there is little information in relation to them being used for latent heat storage applications. This paper presents and analyses the binary salts of NaNO₃–LiNO₃ (46–54%) and NaNO₃–LiNO₃ (40–60%), which are studied to assess their potential to be used for latent heat storage applications. They have the same component materials but with different mixing ratios. Their thermal properties and thermal repeatability over different numbers of cycles were measured using a DSC. The binary salt of NaNO₃–LiNO₃ (46–54%) showed a better thermal repeatability than the NaNO₃–LiNO₃ (40–60%) binary salt. The thermal and chemical stability were tested in the TGA. They both showed good chemical stability below 450 °C.

2. Material preparation and test procedures

2.1. Material preparation

The material preparation procedure is a crucial factor determining the quality of the binary salt. Two methods can be used for the preparation of a binary salt, called direct mixing and indirect mixing. Sometimes, the direct mixing procedure in which materials are mixed in the solid states may result in uneven characteristics. In the current research, indirect mixing was used for the binary salt preparation. To get an even binary salt, NaNO₃ (99%, ASC reagent, provided by Fisher Scientific) and LiNO₃ (99%, Technical, provided by Leverton–Clarke Ltd) were heated at 150 °C for 30 min to fully evaporate the moisture from the sample. The components were then weighed quickly to minimise the influence of any water absorption from the atmosphere. The component materials with the exact mole proportion required were then dissolved in water separately. The solutions were subsequently mixed together and the mixture was placed in an oven kept at 150 °C until all of the water evaporated, leaving a crystal-like mixture. Finally, the crystal-like salt mixture was ground into a powder in a mortar using a pestle.

2.2. Test equipment

A TA Instruments Discovery DSC [18] was used to measure the thermal properties and thermal cycling repeatability of the binary salts. The working temperature range of the DSC is from –180 °C to 725 °C. The precision of the temperature and enthalpy measurements is to accuracies of ±0.005 °C and ±0.04% respectively. All of the tests were conducted under an atmosphere of pure nitrogen.

A TA Instruments Discovery TGA [19] with a Residual Gas Analysis (RGA) was used to test the thermal and chemical stability of the binary salts. The TGA can work up to 1200 °C; the heating rate can be set to be from 0.1 to 500 °C/min. The weight loss and temperature are recorded to within an accuracy of 0.01% and 0.1 °C respectively. All of the tests were made under an atmosphere of pure nitrogen. The coupled RGA was used to monitor the chemical species evolved in to the nitrogen gas environment and determine if some components of the salt mixture changed during the heating cycles.

2.3. Experimental test procedure

The thermal properties of the binary salts, including phase transition temperature (melting and solidification) and latent heat capacity, were measured using the DSC. For each experiment, a sample with a weight of 10–15 mg was heated from 50 °C to 300 °C then cooled back down to 50 °C at the same heating/cooling rate. This was repeated 10 times to allow the effects of absorbed moisture on the initial cycle to be discounted. The three heating/cooling rates used were 5 °C/min, 10 °C/min and 15 °C/min, which enabled the evaluation of the effect of heating/cooling rate on the salts thermal properties. The thermal repeatability of the binary salts performance under multiple cycles was also tested using the DSC. The samples were heated up and cooled down 51 times between 50 °C and 300 °C at a rate of 10 °C/min. The transition temperature and latent heat for each cycle were recorded.

The thermal and chemical stability of the binary salts were assessed in the TGA. The binary salt samples (around 5 mg) were heated from 50 °C to 300 °C then cooled down to 120 °C. The samples were then heated up to 300 °C and cooled down to 120 °C at a constant heating/cooling rate of 15 °C/min for 51 times. The results of weight loss vs. temperature for all 51 cycles were recorded so that the thermal stability of the binary salts could be assessed. To test the salt mixtures chemical stability, the samples (around 5 mg) were heated up to 500 °C at a heating rate of 15 °C/min with isothermal stages at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C of 3 h to obtain details of weight loss resulting from long-term exposure to relatively high temperatures.

3. Results and discussion

3.1. Phase diagram

The phase diagram of the binary sodium/lithium nitrate salts from the literature is shown in Fig. 2. The result from Factsage [20] shows a eutectic composition of 46% NaNO₃ and 54% LiNO₃ at a temperature of 195 °C. Vallet [21] found the eutectic point for this mixture was at 193.8 °C. From the tests undertaken by Maeso and Largo [22], the eutectic point occurred at 45% NaNO₃ and 55% LiNO₃ with a melting temperature of 201 °C. Their results might be slightly affected by the accuracy of the equipment available in the 1990 s. Therefore, in our experiments, the binary salt of 46% NaNO₃ and 54% LiNO₃ was selected as it is very close to the eutectic composition. The second binary salt of 40% NaNO₃ and 60% LiNO₃ was investigated, firstly to address the thermal potential of both mixtures for latent heat storage and secondly to see the effect of the mole percentage of LiNO₃.

3.2. Thermal repeatability

Since the heating/cooling rate can affect the phase transition temperature, three heating/cooling rates were used in the experiments, 5 °C/min, 10 °C/min and 15 °C/min. Fig. 3 shows the effects of heating/cooling rate on the phase change process. The
onset melting temperatures for all three cycles were almost the same, reducing slightly for higher heating/cooling rates. For both binary salts, the lower heating/cooling rate resulted in a smoother phase change curve and a narrower phase change transition range.

An important criterion for the evaluation of a PCM is its long-term stability under cycling, which is called the thermal repeatability. A promising PCM must be able to melt and solidify with a constant phase change temperature and a constant latent heat after hundreds if not thousands of cycles. In the current experiment, the binary salt samples, NaNO$_3$-LiNO$_3$ (46–54%) and NaNO$_3$-LiNO$_3$ (40–60%) were heated up and cooled down between 50 °C and 300 °C at a rate of 10 °C/min for 51 times. The binary salt samples are hygroscopic with water-soluble characteristics. Although precautions to avoid moisture absorption were taken when preparing the salts, this might lead to slight error in weight measurements which would influence the experimental results. Therefore, all of the results exclude the first few cycles in which moisture was driven from the binary salt samples. The average melting temperatures of the binary systems were 193.87 °C and 193.27 °C respectively. The average latent heats of the samples were 261.7 kJ/kg and 244.1 kJ/kg. The results seem to be slightly different compared with the phase diagram by FactSage. However, similar results were found in the literature [17]. The reasons for the differences might be i) the purity of the materials, different chemical contaminants in the materials could affect the result; ii) the phase diagram is calculated using empirical coefficients of enthalpies of mixing, the empirical coefficients were obtained from previous tests and some assumptions were made in their calculation.

The deviations of the measurements of melting temperatures and latent heats from the average were calculated using Eqs. (1) and (2) to determine the difference between each measurement value and the average value. Figs. 4 and 5 show the deviations of the measured melting temperatures and latent heats in the experiments for the two binary salts tested. The binary salt of NaNO$_3$-LiNO$_3$ (46–54%) showed a very good repeatability for both melting temperature and latent heat, especially after the first ten cycles. The repeatability of measurements for the NaNO$_3$-LiNO$_3$ (40–60%) salt was not as good as the NaNO$_3$-LiNO$_3$ (46–54%) salt. However the deviation of the measured melting temperature was within ±0.5% and the deviation of the latent heats was within ±4%, which is still reasonable for a molten salt mixture to be used as a PCM.

$$T_n = \frac{T_n - T_{average}}{T_{average}} \quad 1 \leq n \leq 50$$  

$$L_n = \frac{L_n - L_{average}}{L_{average}} \quad 1 \leq n \leq 50$$  

3.3. Thermal stability

The purpose of the current research is to develop a suitable binary salt for application in solar thermal or industrial waste heat storage at medium temperatures. The thermal stability of the binary salts in the range between 120 °C and 300 °C is very important since a huge amount of heat is available within this temperature range. An experiment to assess this was performed using a TGA with salt mixtures subjected to 51 cycles between 120 °C and 300 °C at a heating/cooling rate of 15 °C/min. The weight loss curves for the two binary salts are plotted in Fig. 6. There was a large weight loss in the first cycle for both mixtures because of their hygroscopic properties. This initial weight loss was attributed to the loss of absorbed moisture. In the subsequent 50 thermal cycles, the weight loss was negligible compared to that of the first cycle. Fig. 7 presents the weight loss percentage for each cycle. The binary salt of NaNO$_3$-LiNO$_3$ (46–54%) showed better thermal stability than NaNO$_3$-LiNO$_3$ (40–60%). From Fig. 7(b), it can be seen that minor weight loss occurred in some cycles. A possible reason for the apparent weight gain in some cycles could be the absorption of moisture from the nitrogen atmosphere (if it was not completely dry). The higher percentage of LiNO$_3$ in the mixture which has good moisture-pickup characteristics leads to a greater weight increase. The other possible reason for this might be the
accuracy of the weight loss recording of the TGA, which is 0.01%. In summary, of the two binary salts, the binary salt with less LiNO₃ had better thermal stability. After 50 cycles, the total weight losses of the binary salts were 0.28% for NaNO₃–LiNO₃ (46–54%) and 0.33% for NaNO₃–LiNO₃ (40–60%) respectively, both of which are considered to be very good. The results of these experiments also confirm the suitability of the two binary salts for thermal energy storage applications under 300 °C in terms of their thermal stability.

3.4. Chemical stability

The thermal decomposition temperature of a PCM is important if it is to be used in a heat storage system. The PCM will lose its original thermal properties above the decomposition temperature and nearly all decomposition processes are not reversible. To assess this, a high temperature stability test was undertaken using the TGA to determine at what temperature decomposition would occur. The mixtures were kept isothermal at 120 °C for 10 min to evaporate the absorbed moisture. The mixtures were then heated at a heating rate of 15 °C/min and kept isothermal at temperatures of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C, for 3 h to measure their weight losses. Fig. 8 shows the results of the experiments for the two binary salts. There was minimal weight loss during the heat up process below 450 °C, a large weight loss occurred at 500 °C. LiNO₃ thermally decomposes as shown by Eq. (3), whilst, NaNO₃ does not decompose completely, producing NaNO₂ and oxygen without nitrogen dioxide, as shown by Eq. (4).

$$4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2 \quad (3)$$

$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2 \quad (4)$$

Table 1 details the percentage weight loss for each binary salt at each temperature. The total weight loss from 250 °C to 350 °C was about 0.07% for NaNO₃–LiNO₃ (46–54%) and 0.11% for NaNO₃–LiNO₃ (40–60%). The weight losses at 450 °C increased for both binary salts, with both being over 0.1%. At 500 °C, there were large increases in weight losses for both mixtures, 7.4% for NaNO₃–LiNO₃ (46–54%) and 8.8% for NaNO₃–LiNO₃ (40–60%). This indicates that the binary salts had started to decompose at 500 °C. Both binary salts worked well below 450 °C but were best under 400 °C. This is significantly higher than the target operational temperature of 200 °C and meets the stability requirement for use in medium temperature heat storage.
3.5. Specific heat capacity

A latent heat storage system normally works in a temperature range, from \(T_1\) to \(T_2\), rather than at a constant set temperature. The heat storage capacity of the system can then be calculated using Eq. (5).

\[
Q = \int_{T_1}^{T_2} C_p \, dT + H_m + \int_{T_1}^{T_2} C_p \beta \, dT \quad (\text{kJ/kg})
\] (5)

Based on DSC test results, the specific heat, \(C_p\), can be calculated from Eq. (6).

\[
C_p = \frac{q}{\beta}
\] (6)

where \(q\) is the unit heat flow (w/g) and \(\beta\) is the heating rate (°C/min). The operating temperature of a medium temperature latent heat storage system is between 120 °C and 300 °C, thus the specific heat in this temperature range is of importance. Fig. 9 shows the specific heats of the two binary salts as a function of temperature above and below phase change. The correlations between the specific heat and temperature for the two binary salts are shown in the following equations.

\[
\begin{align*}
\text{NaNO}_3-\text{LiNO}_3/(46\%–54\%) \quad & \quad \begin{cases} 
C_p &= 1.3175 + 1.568 \times 10^{-3}T (100°C - 180°C) \\
C_p &= -1.8387 + 0.03T - 5.579 \times 10^{-3}T (210°C - 300°C)
\end{cases} \quad (\text{kJ/kg.K})
\end{align*}
\] (7)

\[
\begin{align*}
\text{NaNO}_3-\text{LiNO}_3/(40\%–60\%) \quad & \quad \begin{cases} 
C_p &= 1.2531 + 2.1 \times 10^{-3}T (100°C - 180°C) \\
C_p &= 1.0859 + 3.422 \times 10^{-3}T (210°C - 300°C)
\end{cases} \quad (\text{kJ/kg.K})
\end{align*}
\] (8)

It is well known that a high specific heat is important for sensible heat storage when using molten salts. For latent heat storage, the sensible heat storage should not be neglected. For the two binary salts studied, the heat storage capacity between the melting temperature and 300 °C could be over 210 kJ/kg for molten NaNO\(_3\)-LiNO\(_3\) (46–54%) and over 190 kJ/kg for molten NaNO\(_3\)-LiNO\(_3\) (40–60%).

4. Economic impact

The cost of each component of the binary salts is important since it will affect the overall cost of the heat storage system and its financial viability. NaNO\(_3\) is widely used in the Solar Salt and Hitec Salt which are used either as HTF or as sensible heat storage materials. It is available in large quantities at a very low price. The commercial price of NaNO\(_3\) is around $0.41/kg [23]. Based on cost
NaNO₃ is a promising component to use in producing a low cost PCM. Lithium is considered as a ‘critical material’, which is important to the clean energy economy and with risk of supply disruption [24]. For latent heat storage, LiNO₃ has been investigated for applications in low-temperature heat storage systems with an operating temperature below 100 °C. The commercial price of LiNO₃ is $4.32/kg [25]. Based on the commercial costs of the two salts used in the binary salts, the prices for the two binary salt mixtures studied are $2.32/kg for NaNO₃–LiNO₃ (46–54%) and $2.64/kg for NaNO₃–LiNO₃ (40–60%), respectively.

Compared to the costs of some molten salts used currently for sensible heat storage, the prices of the materials themselves are not advantageous. The demand for LiNO₃ is however increasing greatly and the technology for producing LiNO₃ is also improving. According to a study by Zhao and Wu [25], LiNO₃ could be produced at much lower cost by producing it from lithium carbonate using nitric acid. The overall cost of a heat storage system does not only include the cost of the PCM but also the cost of the supporting systems and materials, such as the heat storage container and the heat exchanger. Due to the higher energy density a latent heat storage system is usually of a smaller size than a sensible heat storage system, which can significantly reduce the cost of the supporting materials. The operating temperature for the studied materials are for a latent heat storage system application between 120 °C and 300 °C, the requirements for some supporting components will be lower when compared to a sensible heat storage system with a large operating temperature range, possibly leading to an overall cost reduction.

5. Conclusions

In this paper two binary salts comprised of NaNO₃–LiNO₃ were studied to determine their potential for use as PCMs for medium temperature latent heat storage. The melting temperatures measured for NaNO₃–LiNO₃ (46–54%) and NaNO₃–LiNO₃ (40–60%) were 193.87 °C and 193.27 °C in the experiments respectively; both have an appropriate melting temperature for medium temperature heat storage. The experiments showed that a lower heating/cooling rate can slightly affect the onset melting temperature and result in a
smoother phase change curve and a narrower phase transition range. Both binary salts exhibited excellent thermal cycling repeatability and thermal stability. The binary salt of NaNO₃–LiNO₃ (46–54%) showed a slightly better thermal performance than the binary salt of NaNO₃–LiNO₃ (40–60%) probably due to the effect of the higher weight percentage of LiNO₃. Both binary salts work well below 450 °C but start to decompose above 450 °C.

The addition of LiNO₃ to NaNO₃ can lower the melting temperature and increase the specific heat (latent and sensible heat). If over half the weight of the mixture is LiNO₃, this will be the best. Subject to improvements in the manufacturing process for LiNO₃, reduced cost and availability, this critical material will be a key component for use in binary salts for PCMs with melting temperatures of approximately 200 °C.

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