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A study of a eutectic salt of lithium nitrate and sodium chloride (87–13%) for latent heat storage

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ABSTRACT

Latent heat storage in salt mixtures has attracted much attention as it can store a large amount of heat within a small temperature range in a small volume compared to sensible heat storage. In this paper, the eutectic salt of $LiNO_3$–NaCl (87–13%) was investigated to evaluate its potential for latent heat storage for medium temperature range applications (< 300 °C). The eutectic salt was prepared using the indirect mixing method. Its thermal properties including melting temperature and latent heat were measured over multiple cycles using Differential Scanning Calorimetry (DSC). The measurements show that the eutectic salt of $LiNO_3$–NaCl (87–13%) has a suitable melting temperature (around 220 °C) and a relatively high latent heat (> 290 kJ/kg). Its thermal decomposition temperature was tested using a Thermogravimetric Analyser (TGA). The salt mixture exhibits an excellent chemical stability below 400 °C with no changes after tests of multiple cycles with DSC and TGA. The main factors affecting the economic feasibility for this eutectic salt were also discussed.

1. Introduction

The industrial sector in the UK is one of the most energy-intensive sectors as it accounts for 25% of the final energy demand, of which 70% is heat production [1]. It is becoming increasingly important to use renewable energy resources and new technologies to make energy use more efficient and sustainable as well as to reduce CO_2 emissions. It is known that when producing heat for industrial processes there is also a penalty in terms of waste heat. The potential and technologies required for industrial waste heat reuse have been investigated and reported in the literature [2–5]. Based on temperature, the industrial waste heat sources can be divided into three groups: high-temperature (> 300 °C), medium-temperature (120 °C–300 °C) and low-temperature (< 120 °C). Compared to high-temperature waste heat, medium-temperature and low-temperature sources are more difficult to reuse due to the relatively low energy quality according to the second law of thermodynamics. Heat at such temperatures needs to be efficiently recovered, stored and transported for use.

Thermal energy storage using a salt mixture as PCM may play a key role in industrial medium-temperature waste heat storage because of its suitable phase change temperature and large heat storage capacity. Kenisarin [6] reviewed the investigations and developments of PCMs for thermal energy storage in detail, having summarised the thermo-physical properties of hundreds of salt mixtures in the melting temperature range of 120–1000 °C, including fluorides, chlorides, hydroxides, nitrates, carbonates, vanadates, molybdates, metal alloys and other salts. He concluded that the hydroxide and nitrate materials have suitable phase change temperatures for applications in medium-temperature heat storage. In addition to suitable temperature and high latent heat storage capacity, reasonable thermal conductivity and good chemical characteristics including stability are needed. In this respect, the nitrate materials have a high potential.

Thermal properties investigations of salt mixtures have been carried out by researchers, mostly focuses on them being used as Heat Transfer Fluid (HTF), such as Solar Salt ($NaNO_3$–KNO_3 /60–40%) and Hitec Salt (KNO_3–$NaNO_3$–$NaNO_2$ /53–7–40%) [7,8] (All the percentages in this paper are based on mole percentages). Lopez et al. [9,10] reported that a eutectic salt of $NaNO_3$–KNO_3 (50–50%) having a melting temperature of 223 °C and a latent heat capacity of 106 kJ/kg. The mixture has several desirable characteristics for use as a PCM, such as good thermal and chemical stability, no phase segregation, low cost and low corrosion potential. Zhao et al. [11] tested a $Ca(NO_3)_2$–$NaNO_3$ mixture to determine its potential for latent heat storage. They concluded that a 3:7 mixture has a similar latent heat capacity to the commonly used Solar Salt (around 130 kJ/kg) but available at half the cost. However, the heat capacity of the material still was low for use in a latent heat storage system. The addition of $LiNO_3$ can lower the phase transition temperature and increase the latent heat capacity of the salt mixture.

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Roget et al. [12] reported that the eutectic mixtures of KNO_3–$LiNO_3$ and KNO_3–$NaNO_3$–$LiNO_3$ have latent heat storage capacities of 178 kJ/kg and 155 kJ/kg respectively, which is useful for reducing the size of a thermal energy storage system. Wang et al. [13] found the ternary system of KNO_3–$NaNO_3$–$LiNO_3$ had good short-term and long-term thermal stability and reliability at temperatures below 435 °C. The phase transition temperatures of the ternary systems of KNO_3–$NaNO_3$–$LiNO_3$ with different component material proportions cane be much lower than 200 °C, with some being lower than 150 °C.

For medium-temperature industrial waste heat storage, a PCM with a melting temperature in the range from 120 °C to 300 °C is of great interest. In this paper, results of experiments to evaluate the potential of a eutectic salt of $LiNO_3$–NaCl (87–13%) for use as a latent heat storage material for medium-temperature heat storage are reported. The thermal properties including melting temperature and latent heat of this salt over multiple cycles were investigated using Differential Scanning Calorimetry (DSC). This material's thermal decomposition temperature was also determined using a Thermogravimetric Analyser (TGA). Other thermal properties, such as cycle stability and specific heat capacity were also presented based on DSC and TGA measurements. Thermal conductivity was predicted using a verified method from literatures. To find the suitable materials contacting with the eutectic salt, a simple material compatibility test was carried out between the salt and some commonly used metals, such as copper, stainless steel 304 and stainless steel 316.

2. Material preparation

An indirect mixing procedure was used for the material preparation to get a homogeneously mixed eutectic salt with a uniform composition. $LiNO_3$ (99%, Technical, provided by Leverton–Clarke Ltd) and NaCl (99.5%+, AR, provided by Fisher Scientific) were heated at 150 °C for 30 min to fully evaporate all moisture from the samples. After drying the two components were weighed quickly, to minimise moisture being absorbed from the atmosphere which would distort the measured quantity of material. The measured quantities of materials were then dissolved in water separately to produce solutions which mixed together provided a homogeneous mixture with the required composition of salts. Subsequently the mixture was placed in an oven and kept at 150 °C until all of the water evaporated, leaving a crystal-like solid salt mixture. The crystal–like salt mixture was ground into a fine powder in a mortar using a pestle.

3. Methodology and results

3.1. Phase change temperature and latent heat

The thermal properties including phase change temperature and latent heat capacity were measured with a TA instruments Discovery DSC [14]. The working temperature range of the DSC is from −180 °C to 725 °C. The precision of the temperature and enthalpy measurements is reported to be within ± 0.005 °C and ± 0.04% respectively. All of the tests were conducted under a pure nitrogen atmosphere. In the tests, a sample with a weight of 10–15 mg was heated from 50 °C to 250 °C then cooled back down to 50 °C at a constant heating/cooling rate. The cycle was repeated 10 times to minimise the effects of any absorbed moisture in the sample on the initial cycle. Two heating/cooling rates were used, 10 °C/min and 15 °C/min in order to evaluate the effect of heating/cooling rate on the materials measured thermal properties. The DSC test results for 10 cycles are shown in Fig. 1. The binary salt exhibits excellent charging and discharging in all cycles except for the first cycle which was affected by absorbed water. The phase change temperatures during heating and cooling were almost the same for the same heating/cooling rate. The average phase change temperatures measured during the charging processes were 221.65 °C and 219.92 °C respectively for the two heating/cooling rates, 10 °C/min and 15 °C/min. The measured average latent heat values were 316.5 kJ/kg and 296.5 kJ/kg.

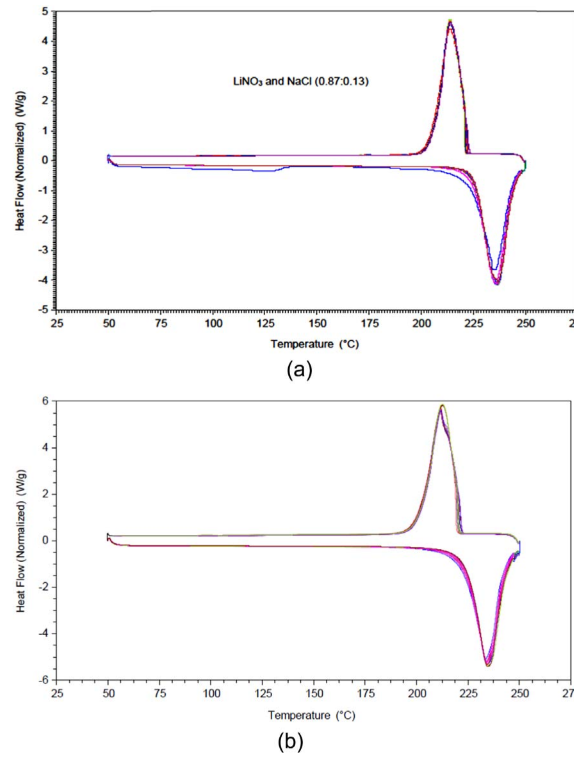

Fig. 1. The measured temperature heat flow graphs for the charging and discharging processes with the DSC (a) heating/cooling rate of 10 °C/min; (b) heating/cooling rate of 15 °C/min.

3.2. Thermal repeatability

A PCM should have a stable phase change temperature and latent heat capacity even after a large number of thermal cycles, which is referred to as the materials thermal repeatability or stability. In the experiments the performed material was thermal cycled 51 times to examine the level of degradation that occurred in the materials thermal properties. During the cycles the eutectic salts were heated up and cooled down between 50 °C and 250 °C with a heating/cooling rate of 10 °C/min. The deviations in the measured melting temperatures and latent heat were calculated from the Eqs. (1) and (2), showing how much difference there is between each test result and the average value. Figs. 2 and 3 show the deviations of the melting temperatures and

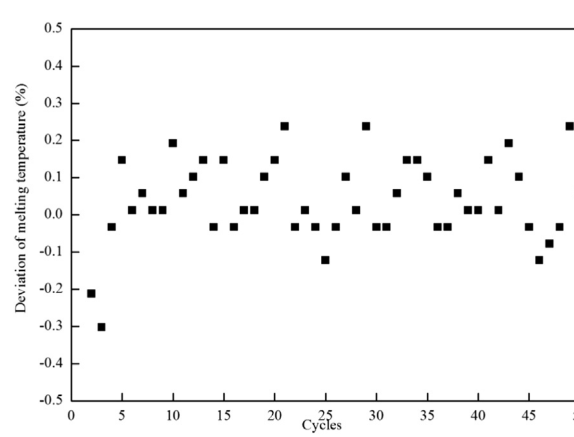

Fig. 2. Deviation of the measured melting temperatures for each cycle from the average value for all cycles in the test.