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Thermal stability of the eutectic composition in $LiNO_3$–$NaNO_3$–KNO_3 ternary system used for thermal energy storage

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ABSTRACT

The new eutectic composition in the $LiNO_3$–$NaNO_3$–KNO_3 ternary salt system has a very low melting point (118 °C) and is a potential candidate for use in parabolic trough solar power generation. The short and long-term thermal stabilities and reliability of the eutectic composition in this ternary system were determined using the Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimetry (DSC), respectively. The system demonstrates excellent short-term thermal stability and reliability during thermal cycling. However, the system showed 8% weight loss during long-term thermal stability test. Long-term isothermal stepwise study reveals that below 435 °C the weight change is minimal and this temperature is taken as the upper limit of thermal stability of the system. The eutectic composition in the ternary system was characterized by XRD and SEM techniques before and after the thermal stability experiments to identify the morphology and compositions of the phases. From the present study it can be concluded that the major contributor to the weight loss is the dissociation of lithium nitrate to lithium oxides.

1. Introduction

Concentrated solar power (CSP) technology is a method of generating electric power from the heat of sun, which is an endless source of clean and free energy. The technology uses mirrors to focus sunlight onto a heat transfer fluid, which in turn converts water into steam that powers a turbine to generate electricity. There are four types of CSP technologies and the two most important types being, parabolic trough and solar power tower. Heat storage and heat transfer are the two most important parameters of a fluid used in the solar power generation. Molten salts are being studied and have been used as potential heat transfer and thermal energy storage media. Low melting point, low density, with moderate heat capacity and thermal conductivity are the important characteristics to be considered in a salt system for thermal energy storage and heat transfer applications. However, thermal stability of the candidate storage media is a very important property that needs to be considered so that long cyclic life is ensured. The development of innovative thermal transfer fluids with high thermal energy storage density is paramount to lower the expenditure of generating electricity [1–4].

Molten nitrate salts have been used as thermal energy storage (TES) media for solar energy applications. They are being extensively used in the solar energy applications due to their low melting point and high thermal stability, which can increase the stable working range [5]. The high heat capacity increases the energy storage density of the heat transfer medium [6,7]. The negligible vapor pressure ensures the steadiness of cyclic service life [8]. Solar salt ($NaNO_3$/KNO_3: 60/40) is the popular salt mixture currently being used as thermal energy storage medium and has a freezing point of 221 °C [9]. A new heat transfer fluid called HITEC®, which is a ternary salt mixture of $NaNO_3$, KNO_3 and $NaNO_2$ is being considered to replace the solar salt because of its low freezing point of 142 °C [10]. Although the melting point for the solar salt is higher than the HITEC® salt, the low cost of the solar salt relative to HITEC® salt promotes the wide usage in solar energy storage applications [8].

Development and synthesis of newer molten salt mixtures with freezing points lower than those currently used for thermal energy storage applications is essential for sustained utilization of solar energy. The approach to developing lower freezing point molten salt mixtures involves systematic investigation of molten salt properties and prediction of new eutectic salt mixtures. Literature review of salt phase diagrams shows that the $LiNO_3$–KNO_3–NH_4NO_3 ternary system possesses a eutectic mixture with freezing point less than 100 °C. However, due to the instability of ammonium nitrate salt at temperatures higher than 300 °C, they are not used in the parabolic trough solar power plant [11,12].

In practical application, the thermal stability is a significant parameter that restricts the use of molten salts as TES media. The thermal stability of solar salt was evaluated at high temperature

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and found to be very stable up to 600 °C in the presence of oxygen [13]. HITEC® salt was found to be stable up to 450 °C in long-term use and up to 528 °C in short-term use [14,15]. Our group recently developed a new eutectic mixture in the $LiNO_3$–$NaNO_3$–KNO_3 ternary system by thermodynamic modeling. The eutectic composition and temperature of the ternary system are $LiNO_3$: 25.9 wt%, $NaNO_3$: 20.06 wt%, KNO_3: 54.1 wt% and 118 °C, respectively [16]. The eutectic temperature of the ternary salt mixture is lower than the solar salt and the HITEC® salt and is a potential candidate for thermal energy storage application. The short-term and long-term thermal stabilities and reliability of this ternary eutectic salt mixture were determined using the Thermogravimetric-Differential Thermal Analyzer (TG/DTA) and Differential Scanning Calorimetry (DSC) techniques. The eutectic salt mixture was characterized for compositional and morphological analysis of the phases using X-ray Diffraction, Scanning Electron Microscopy and Energy Dispersive Spectroscopy techniques.

2. Experimental

2.1. Materials

Eutectic composition in the $LiNO_3$–$NaNO_3$–KNO_3 ternary system was synthesized by mixing corresponding amounts of lithium nitrate ($>$98% pure), sodium nitrate ($>$99% pure) and potassium nitrate (purity 99.0% min) obtained from Alfa Aesar®. All the three salts were used without further purification.

2.2. Thermogravimetric-Differential Thermal Analyzer (TG/DTA)

Perkin Elmer® Pyris Diamond TG/DTA was used to study the short-term and long-term thermal stabilities of the eutectic composition in the $LiNO_3$–$NaNO_3$–KNO_3 ternary system. The photograph of the experimental setup including the data acquisition system is shown in Fig. 1. TG/DTA can be used up to a temperature of 1500 °C. Weight loss and temperature can be recorded in the instrument with an accuracy of 0.0001 mg and 0.01 °C, respectively. It has two weight balance beams, which hold the sample and reference to detect the weight change. The instrument can be calibrated with indium, tin and gold depending on the working temperature range of the study. All the experiments were conducted under high purity argon atmosphere with a flow rate of 200 ml/min and a heating rate of 10 °C/min.

2.3. Differential Scanning Calorimeter (DSC)

Perkin Elmer® Diamond Differential Scanning Calorimeter (DSC) was used to measure the reliability of the eutectic composition in the $LiNO_3$–$NaNO_3$–KNO_3 ternary system. The photograph of the DSC equipment is shown in Fig. 2. The change in eutectic temperature of the salt mixture is recorded during the process of thermal cycling in the temperature of 25 to 350 °C. The working temperature range for the DSC is -50 °C to 700 °C. Endothermic heat flow and temperature can be recorded in the instrument with an accuracy of 0.0001 mW and 0.01 °C, respectively. The measurements were made under high purity nitrogen atmosphere with a flow rate of 20 ml/min and at a heating rate of 5 °C/min.

2.4. Experimental procedure

Short-term thermal stability of the $LiNO_3$–$NaNO_3$–KNO_3 eutectic salt mixture was determined experimentally using TG/DTA instrument. The salts were heated through 5 cycles at 10 °C/min from 75 °C to 500 °C and cooled down. The results are given below in terms of weight loss vs. temperature for 5 cycles. The eutectic salt mixture in the range of 15–20 mg was used for the short-term thermal stability experiments. The procedure for the long-term thermal stability experiments is similar to that of the short-term study. However, instead of heating and cooling sample continuously, the long-term thermal stability study was performed isothermally at constant temperature for 20 h. The experiments were carried out at 200, 350 and 500 °C. At the very beginning, the synthesized sample was left inside the furnace chamber of the TG/DTA at 150 °C for 1 h to remove any absorbed moisture that could have occurred during the process of loading the sample. There is no cooling step involved in the long-term study. After the isothermal holding steps, the furnace was turned off and the weight loss measurements were carried out.

To check the reliability of the ternary eutectic mixture, the salt was treated by repeated thermal cycling in the DSC equipment. 20–25 mg of the sample was used in a standard aluminum pan with lid used for experiments. The sample was held at 200 °C for 2 h to remove the trace amounts of moisture that might be caught in the process of loading sample and also to ensure a homogeneous mixture. The thermal cycling was set between 25 and 350 °C, first by heating cycle at a rate of 5 °C/min followed by a cooling cycle at the same rate. This thermal cycling process is repeated for at least 20 cycles.

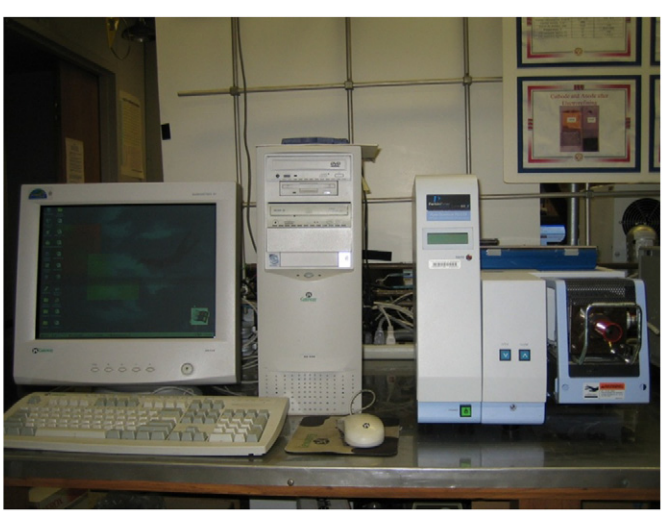

Fig. 1. Experimental set-up of Thermogravimetric Analyzer equipment (TGA).

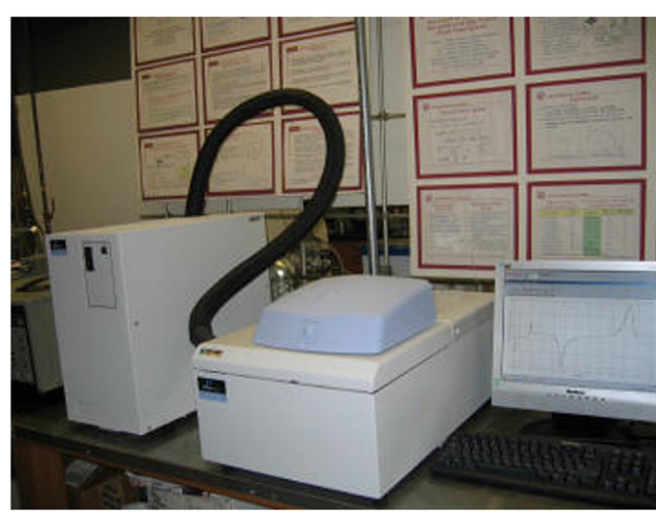

Fig. 2. Experimental set-up of Differential Scanning Calorimetry equipment (DSC).