Solar Energy Materials & Solar Cells 164 (2017) 114–121

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Novel low melting point binary nitrates for thermal energy storage applications

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ARTICLE INFO

Keywords:
Binary molten salt
Thermal stability
Thermophysical properties
Thermal storage materials

ABSTRACT

19 kinds of different ratio of binary mixed molten salt have been formulated, and the formulation of a low melting point binary molten salt has been exploited and its primary thermophysical properties were presented here. The eutectic temperature of the selected binary salt mixture was determined to be 116.9 °C. Further the decomposition point, specific heat, density, viscosity, thermal conductivity and corrosion were determined respectively. Sensible thermal storage cost of the novel eutectic mixture was found to be lower than that of conventional solar salt and HITEC salt. The performance of the binary salt mixture taken at different stages during the test of 1200-h exposure to constant high temperature was discussed based on the results obtained from long-term thermal stability studies. The results show that thermodynamic properties of the molten salt show perfect repeatability before and after the experiments, and most variations rate of the thermal physical properties is within ± 10%, which can be considered as an implication that the candidate has good thermal stability. Therefore, this new kind of binary molten salt thermal storage materials is more competitive and promising to be used in solar power generation systems while providing a comprehensive data for its engineering application and theoretical research.

1. Introduction

Energy is an important material basis of human society's survival and development. With the demand for energy keeps increasing, the contradiction between energy and environment becomes increasingly prominent and has brought new opportunities for renewable energy generation industry, and concentrated solar power (CSP) is considered to be the most promising way for the large-scale use of solar energy in the future since it can be combined with low cost and large scale thermal storage technology and provide continuous and stable adjustable high quality electric energy [1–3]. After decades of research, solar thermal power generation capacity has been developed from the kW level to the MW level, and dozens of solar thermal power plant has been put into operation. The International Energy Agency (IEA) estimates that the capacity of a CSP power station in the world may increase to 147 GW by 2020 and to 1089 GW by 2050 [4].

Thermal storage system is a critical factor to efficiently use the solar energy since it solves the time mismatch between solar energy supply and electricity demand as well as improves the performance and reliability of CSP systems [5]. There are several solar thermal power plants in operation now such as Spain Gemasolar 19 MW and Arcosol 50 MW tower solar thermal power plant [6], and most of them are now employing the molten salt as their HTF and thermal storage media due to its wide temperature range, high heat capacity and energy storage density, low viscosity, low unit cost and so on [7]. These can let more solar thermal power plant to further improve the thermal efficiency, for example, by increasing the operating temperature to improve the efficiency of the Rankine cycle. With the rapid development of solar thermal power generation technology and the increasing demand of large scale energy storage, the development of a new type mixed melt salt with lower melting point, higher stability, better heat transfer and thermal storage characteristics has become the main direction of the study of mixed molten salts.

Murat M. Kenisarin reviews the modern state of art in investigations and developments of high-temperature phase change materials perspective for storage thermal and a solar energy in the range of temperatures from 120 °Cto 1000 °C [8]. From the review, the melting point of nitrate is generally low in common inorganic salts, so it is the most commonly used as potential thermal energy storage and transfer media. Especially, Solar salt (60 wt% $NaNO_3$–40 wt% KNO_3) and Hitec Salt (53 wt% KNO_3, 40 wt% $NaNO_2$ and 7 wt% $NaNO_3$) have been widely used in the heat transfer and thermal storage system for CSP

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http://dx.doi.org/10.1016/j.solmat.2017.02.021
Received 26 September 2016; Received in revised form 14 December 2016; Accepted 13 February 2017
Available online 16 February 2017

and their relative thermal properties are also described in detail [9–13]. However, the former with high melting point and the latter with poor stability can't exhaustively meet the demand of CSP and energy storage diversity, as limits its use. From the point of view of heat storage and commercialization, most current researches mainly concentrate on the properties, the cost and the structure of the nitrate, and have improved the characteristics of molten salt as heat transfer and thermal storage medium. C.Y. Zhao [14] developed binary molten salts composed of $NaNO_3$ and $Ca(NO_3)_2$(3:7) and found that different mixing ratio will lead to different amount of eutectic production, and the melting point of the binary nitrate is about 220 ℃, and that of price is only 65% of Solar salt. However, an auxiliary heater still be needed to maintain the HTF and TES systems above the melting point for freeze protection just as Solar salt.

A lot of researchers have improved the performance of mixed nitrates by introducing additives and changing the proportion of components on the basis of Solar salt and Hitec Salt, etc. A fused salts mixture ($LiNO_3$-KNO_3-$NaNO_3$-$NaNO_2$) and its preparing process and corrosion performance are disclosed by Yu J G, and its optimum operating temperature range is 250–550 ℃ [15]. Tao Wang [16] developed a new low melting point quaternary eutectic mixture consisting of $LiNO_3$, $NaNO_3$, KNO_3 and $2KNO_3{\cdot}Mg(NO_3)_2$ by using thermodynamic principles and was experimentally verified to have a melting point of 373.90 ± 0.78 K. Robert W. Bradshaw [17] used $Ca(NO_3)_2$ as additive added in $NaNO_3$-KNO_3-$LiNO_3$ ternary molten salt to prepare a new quaternary nitrates, and its melting point is below 100 ℃, and its viscosity and short-term thermal stability were also determined. Subsequently, a quinary mixed nitrate has been exploited ($NaNO_3$, KNO_3, KNO_2, $LiNO_3$ and $LiNO_2$) by JG. Cordaro [18], its melting point is about 70 ℃. However, the poor thermal stability of nitrite, no commercially available $LiNO_2$ and complicated preparation method restrict its large-scale promotion and application. Nan Ren [19] developed a new kind of nitrate based on different mixing ratios of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2{\cdot}4H_2O$, and its melting point can be down to below 90 ℃ with their decomposition temperature above 600 ℃. Using this quaternary nitrates as a thermal storage media for HTF and TES of CSP plants can significantly reduce the cost of electricity by eliminating heat exchangers between HTF and TES for high exegetic efficiency and reducing the heat load for the freeze protection. A similar study of other three salts (Na–K–Li, Na–K–Ca, Na–K–Li–Ca) was conducted by Siegel et al. and the thermophysical properties data were also measured [20]. As mentioned above, these formulation are initially developed as heat transfer or thermal storage medium and they have a low melting point or high upper limit temperatures, but such excellent performance as heat transfer and thermal storage medium is not much enough for practice application. Although the addition of lithium nitrate will greatly reduce the melting point of the molten salt, lithium is too expensive to apply as heat storage materials with its prices rising. In CSP, a thermal storage system always needs a tremendous amount of heat storage material, which requires high capital investment costs if using the lithium. Therefore, minimizing the cost is an important criterion for selecting heat transfer fluids while maximizing the heat transfer performance for industrial application. Development and synthesis of newer molten salt mixtures with excellent performance and substantial cost than those currently used for thermal energy storage applications is necessary for sustained utilization of solar energy.

Our laboratory did a series of work to exploit molten salts with low melting point and low cost. In order to obtain molten salts with excellent thermal performance and substantial cost, a new kind of binary molten salts was prepared based on different mixing ratios of KNO_3-$Ca(NO_3)_2{\cdot}4H_2O$. Primary relevant properties of this mixture such as melting point, decomposition temperature, crystallization point, specific heat, density, viscosity, thermal conductivity, corrosion and long-term thermal stability were measured and analyzed comprehensively to determine the feasibility of this binary salt system to be a potential candidate for the solar thermal energy storage applications. Thermodynamic properties such as melting point, latent heat of melting, crystallization point and thermal decomposition temperature of mixed molten salts were measured by Differential Scanning Calorimetry (DSC) and Thermogravimetric (TG) analysis. The density of the selected molten salt was measured by the Archimedean principle. The specific heat of the molten salt was obtained by comparing with standard sapphire with known specific heat using Synchronous Thermal Analyzer (STA). Thermal conductivity of the mixture was measured by the laser thermal conductivity analyzer (LFA). The viscosity of mixed molten salt at high temperature was measured by high temperature viscometer whose principle is means of rotary oscillation. The corrosion rate of stainless steel 316 L immersed in the select binary nitrates at different temperature was measured by weight loss method. The repeatability of thermophysical properties of the sample was determined experimentally in working condition of constant high temperature, and the long-term thermal stability study was obtained.

2. Experimental scheme

In order to obtain molten salts with excellent thermal performance and substantial cost, a new kind of binary molten salts was prepared based on different mixing ratios of KNO_3-$Ca(NO_3)_2.4H_2O$. Thermodynamic properties, including melting point, decomposition temperature, crystallization point, specific heat, density, viscosity and thermal conductivity, and thermal stability were measured.

The experimental scheme is presented as follows:

(1) Preparation of mixed molten salt. All the salts obtained from Beijing Chemical Reagent Factory were at least 99% pure, and the calcium nitrates contain crystallization water molecules. The binary molten salt mixture was prepared by mixing the two salt components(KNO_3-$Ca(NO_3)_2{\cdot}4H_2O$) according to the molar ratio from 0.95:0.05 to 0.05:0.95. Then they are weighted by the mole ratio being transformed into mass ratio and rapidly heated to 500 ℃ after pre-melted to 300 ℃ at 10 K/min in muffle furnace for 24 h to make the mixture melt completely and evenly mixed. Finally the products are naturally cooling down until the salt mixture solidified to a white mass. The solidified salt mixture was then ultrafine pulverized into powder, sealed in corundum crucible with lid and kept in sweatbox to prepare for subsequent experiments.
(2) Optimum selection and STA tests of the molten salt with lower melting point. The mixture is heated from 30 ℃to 500 ℃at 10 K/min heating rate and 500 ℃to 30 ℃ at 5 K/min cooling rate under N_2 purging of 30 mL/min, and this procedure circles three times. DSC tests were carried out on 19 different proportions of binary mixed molten salts. And the system of the solidus and liquidus were obtained respectively by connected the solid phase and liquid phase points of each component as the starting point of the melting peak was used as the solid point, and the termination point of the melting peak was used as the liquid phase point. The phase diagram of the binary system was measured, and the eutectic molten salts with lower melting point were selected to be utilized for further study. And the crystallization point measurement of the selected salts is measured by analyzing the DSC curves.
(3) Decomposition temperature measurement. In order to obtain more complete molten salt decomposition process, the samples were measured with aluminum oxide crucible and heated from 30 ℃to 800 ℃at 10 K/min heating rate. The TG curve of the molten salt selected was determined.
(4) Density measurement. Density is an important physical and chemical property of molten salts, and has its significance in practical and theoretical research. In this paper, the density of the selected molten salt was measured by the Archimedean principle.