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Thermal properties enforcement of carbonate ternary via lithium fluoride: A heat transfer fluid for concentrating solar power systems

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ABSTRACT

A novel eutectic of Li_2CO_3-Na_2CO_3-K_2CO_3 improved by LiF, when employed as a heat transfer fluid in concentrating solar power systems, is prepared to eliminate the disadvantage of limited operating temperature range and low specific heat as well as thermal conductivity. Using the static melting method, Li_2CO_3-Na_2CO_3-K_2CO_3 with 15.0 wt.% LiF which is simply physical mixture determined by X-ray diffraction, is chosen as the optimized candidate. Results indicate that, at 10 °C/min of heating rate, LiF-Li_2CO_3-Na_2CO_3-K_2CO_3 reached melting point of 368 °C and upper temperature limit of 753 °C, allowing it to be effectively employed in thermal storage and heat transfer in high temperature CSP systems. During temperature range from 400 to 600 °C, the liquid quaternary exhibited notably mean specific heat of 1.917 J/(g·°C), which is larger than that of the original ternary eutectic. Thermal conductivity of solid LiF-Li_2CO_3-Na_2CO_3-K_2CO_3 reached the stable level of 1.021 W/(m·°C) at 320 °C. Density of improved eutectic tested by the archimedean principle is approximately 1.95 g/cm^3. In conclusion, LiF-Li_2CO_3-Na_2CO_3-K_2CO_3 can be employed as the admirable heat transfer fluid for thermal storage and heat transfer in high-temperature CSP plants. This investigation will provide useful information for further improvement of molten salt based heat transfer fluids.

1. Introduction

Rapid economic development and continuous population increase require a dramatic supply of power, which is primarily produced from fossil fuels in the current stage. And therefore, the shift from fossil fuels to other green energy alternatives should be a pressing demand due to limited fossil fuel resources, and harmful gas emissions [1–4]. From the perspective of industrial applications on a large scale and cost competitive with respect to conventional energy, it is apparent that solar energy potential is of great interest for the power sectors in areas where receive strongly direct radiation, including Southern Europe, America, North Africa, Middle East, and Southern Asia, as well as Australia, etc [5].

Concentrating solar power (CSP) (also known as solar thermal electricity) technologies is considered as a practical way of using solar energy to generate electricity [1,6,7], featured with flexible and grid-friendly, this technology increasingly becomes a research field where numerous explorations have been conducted. Generating electricity based on a conventional thermodynamic cycle (e.g., the Rankine cycle), CSP can be cost-effectively employed with relatively high efficiency in stand-alone buildings or remote areas where possess sufficient sunshine [8–10].

Since the Rankine cycle will be more efficient under higher operating temperatures, the emerging tower and dish CSP systems, which can be respectively operated in critical condition (550–900 °C) and supercritical condition (700–1200 °C), have increasingly become the novel research focus for generating electricity from solar energy. Hence the high-temperature heat transfer fluid (HTF) is supposed to be a critical component for improving the thermoelectric conversion efficiency of CSP systems [11–13]. Currently, salts are the most promising candidate for upper temperature limit, excellent thermal stability, large heat capacity and low cost. In fact, nitrates are commonly used HTFs in central receiver and parabolic trough CSP plants [9,14–16]. However, they decompose at temperatures above 550 °C [17,18]. Although possessing higher temperature limits, fluorides have larger volumetric

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expansion in the transformation from solid to liquid [14]. On the other hand, chlorates have strong corrosive properties, making it difficult to find the proper material for storage containers or pipelines [19,20]. In this case, carbonates will be of the highest quality molten salt HTFs in CSP.

Among these carbonate salts, ternary of Li_2CO_3-Na_2CO_3-K_2CO_3 is regarded as a superior candidate for high-temperature TES in CSP plants. The eutectic has the lowest melting point of approximately 400 °C under the mass composition of Li_2CO_3:Na_2CO_3:K_2CO_3 = 32.1:33.4:34.5 [21–24]. Furthermore, this salt used as thermal storage medium allows CSP systems to operate highly efficiently than conventionally used plants. Nevertheless, poor thermal properties, such as specific heat and thermal conductivity, severely limit the heat transfer performance, and thus lead CSP plants to be uncompetitive to traditional fossil-fueled power plants. While high melting points and the small heat capacities of carbonates limit the operating temperature range of CSP systems and decrease heat transfer performance when circulation in the heat loop of CSP system [25–27].

Several papers have been reported to determine the potential of carbonate molten salts as HTFs for CSP systems. binary carbonate of Na_2CO_3-K_2CO_3 with a heat capacity of 1.56 J/(g·°C) showed the melting point of 710 °C [21,28]. Byeongnam Jo et al. [29] analyzed another binary carbonate of Li_2CO_3-K_2CO_3 in 14 different composition ratios. Results revealed that the specific heat capacity was strongly dependent upon lithium carbonate. The specific heat drastically increased up to that of pure lithium carbonate in the liquid phase and decreased down to that of pure potassium carbonate in the solid phase. Heat capacity of binary composed by Li_2CO_3 (62.0 mol.%) and K_2CO_3 (38.0 mol.%) with a melting point of approximately 505 °C, were 1.61 and 1.36 J/(g·°C) in the liquid and solid phases, respectively. 36 types of Li_2CO_3-Na_2CO_3-K_2CO_3 with different compositions were prepared, and the melting points and specific heats were measured by means of differential scanning calorimetry [30]. Melting points and specific heat of K_2CO_3 (20 wt.%)-Li_2CO_3 (10 wt.%)-Na_2CO_3 (70 wt.%) were approximately 400 °C and 1.67 J/(g·°C), respectively. Decomposition temperature detected by thermogravimetry analysis was more than 800 °C. Addition of 5 wt.% of Rb_2CO_3 and Cs_2CO_3 reduced the melting temperature of Li_2CO_3-Na_2CO_3-K_2CO_3 by 30 °C without sacrificing the stability at high temperature [31]. Results also indicated that addition of Li/Na/KOH mixture exerted the positive effect of reducing melting point than the addition of the individual hydroxide. Thermal stability would decrease with addition of Li/Na/KOH mixture at high temperature due to the decomposition of LiOH. Wang et al. [32] theoretically designed and experimentally measured LiF-Na_2CO_3-K_2CO_3 for TES unites or metal treatments. DSC determined that melting point of the ternary eutectic was 421.41 °C, while the heat capacity was 1.90 J/(g·°C). The upper working temperature limit, defined with 0.01 mg/min of dTG trace as thermally stability, was approximately 800 °C. Measurements of thermal conductivity, enthalpy together with density, were also engaged in their paper.

Furthermore, our lab has engaged in research for enhancing the thermal properties of carbonates for many years. Li_2CO_3-Na_2CO_3-K_2CO_3 with nano Al_2O_3 were prepared to improve thermal properties for high-temperature heat transfer in CSP systems [26]. The optimized content of Al_2O_3 was 1.0 wt.% of 20 nm Al_2O_3, 1.0 wt.% of 50 nm Al_2O_3 and 0.8 wt.% of 80 nm Al_2O_3. The maximum enhancement of specific heat is 18.50% in solid and 33.01% in liquid, 17.92% in solid and 22.71% in liquid, 13.18% in solid and 17.53% in liquid for nanofluids containing 20, 50 and 80 nm Al_2O_3, respectively. Thermal conductivity is separately improved by 23.29%, 28.46% and 30.88%. Zhang et al. [33] evaluated the thermal properties of Li_2CO_3-Na_2CO_3-K_2CO_3-T-ZnOw through solution-evaporation method. Results indicate prepared composites expressed superior thermal storage capacity and chemical stability and thermal conductivity is approximately 4.483 W/(m °C). Specific heat is 1.357 J/(g °C) for solid and 1.665 J/(g °C) for liquid, respectively.

Previous investigations are primarily focused on preparation and improvement of binary or ternary carbonate eutectics [21–24]. A great number of attempts have been carried out in papers with the purpose of modifying thermal conductivity and specific heat [27,33–37]. Unfortunately, the operating temperature range and thermal properties are still unable to ideally satisfy heat transfer and thermal storage requirements from HTFs. As a high-temperature stable material, LiF possesses outstanding properties due to the presence of lithium ion. According to the heterogeneous nucleation theory, it is expected that the introduction of LiF can produce a positive effect on lowering the melting point of eutectics [3,11]. Additionally, the specific heat and thermal conductivity might be improved owing to the dense heat flux density and high current efficiency of LiF. To the best of our knowledge, modification of ternary eutectics by high-temperature fluoride has not been examined to date. As a result of that, this study aims to fabricate a novel ternary carbonate eutectic improved by the addition of LiF. Properties of improved ternary eutectics, including chemical stability, melting point, specific heat, thermal conductivity and thermal stability as well as density are measured to address the potential as HTFs for the CSP plants. The results also can validate the improvement of specific heat and thermal conductivity because of the introduction of LiF.

2. Materials and methods

2.1. Materials

Lithium carbonate (Li_2CO_3, purity ≥99.0%), sodium carbonate (Na_2CO_3, purity ≥99.8%) and potassium carbonate (K_2CO_3, purity ≥99.0%) were purchased from Kelong Chemical as the carbonate salts. High-temperature additive of lithium fluoride (LiF, purity ≥99.0%) was provided by Aladdin Chemical. Table 1 listed their melting point tested from DSC measurement, boiling point, density and specific heat from the handbook [38]. All the chemicals are of analytical grade and used without further purification.

2.2. Eutectic preparation

The objective of this research is to fabricate and evaluate novel

Table 1
Melting point, boiling point, density and specific heat of LiF, Li_2CO_3, Na_2CO_3 and K_2CO_3.

Materials	LiF	Li_2CO_3	Na_2CO_3	K_2CO_3
Melting point (°C)	849.2	724.6	855.3	898.6
Boiling point (°C)	1670	1342	1600	1333.6
Density (g/cm³)	2.295	2.110	2.533	2.29
Specific heat (J/(g·°C)	$C_p = 0.0022T + 3.9466$, $0 < T < 925$ °C	$C_p = -8 \times 10^{-6}T^2 + 0.013T + 0.4776$, $325 < T < 875$ °C	$C_p = 0.0023T + 2.3133$, $20 < T < 935$ °C	$C_p = 0.0018T + 1.9681$, $350 < T < 950$ °C