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Thermophysical properties enhancement of ternary carbonates with carbon materials for high-temperature thermal energy storage

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ABSTRACT

Ternary carbonates in the form of Li_2CO_3-Na_2CO_3-K_2CO_3 enforced by expanded graphite, graphene nanosheets and multi-walled carbon nanotubes are originally prepared though the solution-evaporation with the purpose of enhancing heat transfer for employment in concentrating solar power. FT-IR, XRD and SEM results indicate that three carbon materials are physically dispersed into composite carbonates with the effect of supporting structural support as well as improved thermal properties. The presence of carbon materials presents a slight effect on the melting and freezing temperature of ternary carbonates. It is apparent that enhancement of carbon materials on the heat transfer of the composite carbonates is mainly manifested in the aspect of thermal conductivity improvement. Expanded graphite, graphene nanosheets and multi-walled carbon nanotubes show respectively the enhancement of approximately 59.1%, 32.9% and 24.8% on average to thermal conductivity. Carbon materials also illustrate obvious improvement on the specific heat and the strengthening effect of liquid composite carbonates is generally better than that of solid carbonates. Average specific heat of composite carbonates modified by expanded graphene, graphene nanosheets and multi-walled carbon nanotubes is 1.278, 1.322 and 1.299 J/(g·°C) for solid and 1.502, 1.638, and 1.533 J/(g·°C) for liquid, respectively. Additionally, prepared composite carbonates exhibit superior cyclic stability and it is concluded that composite carbonates with carbon materials as effective latent heat storage materials will have great potential for application in thermal energy storage in terms of satisfactory thermal properties.

1. Introduction

Development of renewable energy production should be urgently taken into consideration with radical climate change and increasing environmental deterioration throughout the world which are primarily caused by the excessive combustion of fossil fuels for large-scale electrical grids (Hang et al., 2008; Kuravi et al., 2013). Among the various possible electricity generation approaches using renewable energy, concentrating solar power (CSP) has the significant advantage of high efficiency, plentiful recourse as well as convenient operability. However, efficiency improvement and cost reduction have been identified the primary techno-economic challenge associated with the development of commercial-scale CSP due to the intermittence of solar radiation (Dorcheh and Galetz, 2016; Liu et al., 2016; Prieto et al., 2016; Xie et al., 2011). Integration of thermal energy storage (TES) is believed to be an efficient strategy for eliminating the mismatch in time and space between the supply and demand of the solar energy. TES temporarily reserves the excess thermal energy collected from heliostats when CSP plants are in a relatively low load. Furthermore, it also has the ability of supplying stored heat for CSP plants during times of peak load or in the insufficient sunshine conditions. Therefore, TES can effectively maintain the uninterrupted generation of CSP plants and continue to supply power to residential and industrial grids (Tian et al., 2016; Kuravi et al., 2013; Liu et al., 2016; Madathil et al., 2016).

Latent heat TES which storages energy by physical state change of phase change materials (PCMs) exhibits desirable superiority relative to sensible energy storage or chemical energy storage due to the large energy storage density and constant temperature during storage. Molten salts with high melting point, excellent thermal stability and low vapor pressure have drawn a great deal of worldwide attention (Wang et al., 2010; Brosseau et al., 2005; Pan et al., 2016). Among these molten salts, ternary carbonate of Li_2CO_3-Na_2CO_3-K_2CO_3 is regarded as a superior candidate for high-temperature latent heat TES in CSP plants, due to its low melting point of approximately 400 °C and large thermal storage

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capacity. However, the Li_2CO_3-Na_2CO_3-K_2CO_3 compounds typically have undesirable thermal properties, especially in thermal conductivity, limiting their further deployment in large-scale applications (Fan and Khodadadi, 2011; Li et al., 2017; Mao, 2016).

Charging and discharging rates of TES are significantly restricted by the low thermal conductivity and various aspects of attempts to enhance the performance have been performed. Generally, there are four common enhancement methods for thermal conductivity. (1) Enlargement of heat transfer surface, such as adding tubes, fins or metal foams. An electronic passive thermal management system was designed with a hybrid heat sink which had parallel fins sintered onto the top and copper metal foam-paraffin composite saturated in a hollow basement (Qu et al., 2012). Results showed that copper foam reduced the surface temperature and the time required to reach the melting point of the paraffin. (2) Improvement of PCMs thermal performance, such as adding high thermal conductivity nanoparticles or carbon materials. The specific heat of Li_2CO_3-K_2CO_3 in the presence of nano-silica and alumina by weight with 5, 10, 30 and 60 nm of average size was examined (Dudda and Shin, 2013). Investigations showed that there were increase of approximately 25.0% and 33.0% in the specific heat for silica and alumina at the weight concentration of 1.0%, respectively. The thermal properties of Li_2CO_3-K_2CO_3 were improved by carbon nanomaterials (Tao et al., 2015). Graphene sheets and single-walled carbon nanotube were the best additives to enhance specific heat and thermal conductivity, which could be respectively enhanced up to 18.6% and 56.9%. (3) Enhancement of heat transfer uniformity, such as using multistage PCMs. The effects of multiple PCMs and single PCM configuration for thermal energy storage were compared at a pilot plant scale (Peiró et al., 2016). Effectiveness enhancement in multiple PCM was approximately 19.4% compared to the single PCM configuration. (4) Microencapsulation. micro-encapsulated PCMMs were prepared with α-Al_2O_3 as the shell and Al-25 wt.% Si as the core for high temperature applications (Nomura et al., 2009). The composites exhibited excellent durability up to 300 cyclic stability cycles and the heat capacity was five times higher than that of conventional solid sensible heat storage materials.

Based on the above reviews, the majority of the reported literature has been confined to low-temperature organic PCMs (mainly paraffin or fatty acids) and high-temperature hydrated salts, nitrates, binary carbonates or metal alloys. Furthermore, limited efforts have been devoted to the solution of ternary carbonates. Furthermore, thermal properties of ternary carbonate which are available both in the experimental and industrial stages used for TES are still unable to satisfy the heat transfer demand in accuracy of practical application. In addition, due to the high temperature of applied environment and technical limitation, conventional methods for enhancement thermal properties, such as metal tubes, fins or metal foams, multistage PCMs and micro-encapsulation are difficult to achieved. As to nanoparticles, the dispersibility and cyclic stability remain touchy issues for application to ternary carbonate.

With an excellent thermal conductivity of 129 W/(m·K) and stability for carbon materials, numerous experimental investigations and numerical simulations associated with carbon materials have been conducted for low temperatures PCMs, nitrates and binary carbonates (Olivares, 2012; Singh et al., 2015; Tao et al., 2015; Tiari et al., 2016; Zhao et al., 2016). Results consistently maintain that the addition of carbon materials yields excellent improvement to thermal conductivity of matrix. Similarly, it can be theoretically speculated that the thermal conductivity of ternary carbonates will exhibit enhancement when carbon materials are added (Al-abidi et al., 2013; Izquierdo-Barrientos et al., 2015; Singh et al., 2015; Yang and Garimella, 2010; Zhang et al., 2017). On one hand, this study aims to prepare composite ternary carbonates with the introduction of three carbon materials for high-temperature TES. These carbon materials are expanded graphite (EG) with three-dimensional structure, graphene nanosheets (GNSs) with two-dimensional structure and multi-walled carbon nanotubes (MWCNTs) with one-dimensional structure, respectively. On the other hand, detailed experimental analysis of thermal properties, structural and morphology determination are also provided to illustrate the effect of three different carbon structures to thermal properties. Finally, the cyclic stability determination is accomplished by melting/freezing circles in DSC apparatus.

2. Materials and methods

2.1. Materials

Anhydrous lithium carbonate (purity ≧99.0%), anhydrous sodium carbonate (purity ≧99.8%) and potassium carbonate (purity ≧99.0%) purchased from Kelong are selected to prepare ternary carbonate salts. Deionized water is provided from Aladdin with conductivity of less than 0.1 µs/cm. Sodium dodecyl sulfate (purity ≧85.0%) is obtained from Kelong Chemical Co. All the chemicals are of analytical grade and used without further purification.

The three carbon materials embedded in the modification of composite salts are expanded graphite (EG) with three-dimensional structure, graphene nanosheets (GNSs) with two-dimensional structure and multi-walled carbon nanotubes (MWCNTs) with one-dimensional structure.

The microwave expansion method is employed to prepare EG. Expansible graphite (size = 80 mesh, carbon content = 99%, density = 1.1 g/cm^3, expansion coefficient = 200 mL/g) purchased from Qingdao Jinrilai, is placed in a 50 °C of drying oven for 24 h before usage. 1.0 g of expansible graphite after drying is transferred to a ceramic crucible and heated in a microwave oven for the preparation of EG. The microwave power and expansion time are 700 W and 30 s, respectively. In addition, GNSs (content >99.5%) are provided from Ningbo Morsh and MWCNTs (carbon content = 98%, —OH content = 1.76%) are purchased from Chengdu organic chemistry co., LTD.

The specific surfaces of the three carbon materials were characterized using a surface area & pore size analyzer (ASAP 2000 Micromeritics) with nitrogen isothermal adsorption. The five-point Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area. Prior to conducting the BET measurement, the samples were outgassed at 150 °C for one hour to eliminate possible volatile adsorbents. Table 1 lists the structure and geometric parameters for the three carbon nanomaterials.

Table 1
Structure and geometric parameters for three carbon materials.

Materials	EG	GNSs	MWCNTs
Structure	Space, 3D	Square sheet, 2D	Short cylinder, 1D
Diameter/thickness	0.2–20 mm	4–20 nm; layers <20	Outside: 20–30 nm; inside: 5–10 nm
Length	50–150 mm	5–10 mm	10–30 µm
Specific surface area	19.785 m^2/g	1837.657 m^2/g	413.872 m^2/g