

Preparation of binary eutectic chloride/expanded graphite as high-temperature thermal energy storage materials



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ABSTRACT

Binary eutectic chloride (NaCl–CaCl₂)/expanded graphite (EG) composite phase change materials (PCMs), used as high-temperature thermal energy storage materials, were prepared by an impregnating method, and the effects of EG additives on thermal properties of compound salts were investigated by TEM, DSC and Hotdisk techniques. The results revealed that both the specific heat capacity and phase change latent heat of composite PCMs decreased with the increase of EG content, the variation of phase change temperature was negligible, and the thermal conductivities of composite PCMs increased linearly with the addition of EG content and density. In particular, the thermal conductivity of the composite PCM with 20 wt% of EG and 2 g/cm³ of density was 4.937 W/(m K), which showed 701.1% higher than binary eutectic chloride. The heating and cooling rate of composite PCMs were higher than binary eutectic chloride, and the melting and freezing platform time also reduced with the addition of EG content.

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1. Introduction

With the rapid development of modern industrial society, the shortage of energy sources has been realized as an obstacle for future development. Nowadays, fossil fuels are still major energy resources, but various renewable energies have been showing more and more attraction because of its no-harm to environment and abundant storage [1–3]. Most renewable energy fluctuates strongly with time and environmental conditions, and thermal energy storage system can collect the redundant energy and release whenever needed, which balance the mismatch between energy supply and demand. Thus, thermal energy storage and transportation are crucial for any renewable energy system, which is especially important for improving thermal energy utilization efficiency [4]. In comparison with sensible heat storage, latent heat storage has the advantage of a high heat storage density due to the enthalpy of fusion. Because phase transition occurs at almost constant temperature, the storage system has a quite small temperature variation.

Recently, molten salts are considered as ideal media for high-temperature heat storage and transfer with the desirable features including broad operating temperature, high thermal capacity,

low-cost, good thermal/chemical stability, low vapor pressure and viscosity [5–9], and two commercial salts have been presented and applied in concentrating solar power (CSP) plants [10,11]. However, molten salt has a major disadvantage of low heat charging and discharging rates due to its low thermal conductivity in energy system, which might result in local overheat and crash problems for the consideration of system safety and stability. So far, there are various methods carried out to enhance heat transfer in energy storage systems, including adding finned configurations [12], dispersing high conductivity particles (metal, ceramic, graphite, graphene, CNT, et al) [13–19], impregnating a porous matrix (metallic or carbon) [20,21] and encapsulating material [22]. Among them, expanded graphite (EG) with porous structure has been realized as an excellent heat fortifier to improve thermal conductivities of materials. EG is easy to be obtained from graphite flakes, achieving a high external heat transfer coefficient, low bulk density, strong resistance to corrosion and chemical stability. Usually, there are two methods to incorporate PCMs with EG: direct blending of PCMs with EG and impregnation of molten PCMs in porous material [23]. By comparison, the latter is more simple and efficient for fabrication. Fused PCMs are inhaled into EG pores because of capillary effect, which has larger thermal conductivity than direct blending. Meanwhile, another advantage for impregnation method is no liquid leakage during its phase transition. Pincemin S. et al. [16] elaborated the nitrates (NaNO₃, KNO₃ and their eutectic)/EG composites by dispersion of graphite within molten salts leading to an intensification of thermal

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conductivities, which decreased at increasing temperature and the thermal conductivity intensification factor was equal to 10 for an effective conductivity of 6 W/(m K) close to the melting point. Lopez Jérôme et al [24] studied graphite/salt composites by isotropic compression of an initial mixing of ground expanded graphite flakes (500 μm mean size) and $\text{KNO}_3/\text{NaNO}_3$ (50 mol%). A poro-thermo-elastic analysis was carried out for understanding melting behavior of composite materials. Increasing porosity (voids) within the graphite matrix skeleton reduced its rigidity and to increase the pore wall thickness, which led to a reduction of the effective thermal conductivity. Zhao C.Y. et al. [25] investigated the feasibility of expanded graphite to enhance the heat transfer of NaNO_3 , and it was found that EG could enhance the heat transfer in the solid region, but suppress the natural convection effect in the liquid zone, which reduced the temperature difference among the PCMs and shortened the charging/discharging period.

Most of the related research focused on low melting-temperature PCMs ($\leq 400^\circ\text{C}$). However, it is necessary to study the performance of high temperature ($> 400^\circ\text{C}$) PCMs for higher efficiency of systems in the heat storage of CSP or industrial waste heat recovery. Chlorides molten salts are attractive candidates owing to high melting point, latent heat and thermal conductivity. In addition, there are huge amount of waste chloride salts in Chinese salt lake without any usage, which will significantly decrease energy storage material cost. Oztekin Alparslan et al [26,27] selected MgCl_2 and eutectic NaCl-MgCl_2 as storage media with phase change and used cylindrical steel shells to encapsulate the PCM, which can store thermal energy up to 450°C for CSP systems. However, more work still need to be done for developing chlorides molten salts applied in high-temperature heat storage system.

In this paper, binary eutectic chloride (NaCl-CaCl_2) was chosen as high temperature ($\geq 400^\circ\text{C}$) heat storage medium, and EG was adopted to enhance the heat transfer performance of heat storage system. Composite PCMs were prepared by impregnation of molten eutectic NaCl-CaCl_2 in porous EG. The thermo-physical properties were measured to evaluate its potential application, including melting/freezing temperatures, latent heat, and specific heat capacity. Especially, the apparent thermal conductivity of the pure binary chloride and chloride/EG composites were compared, and the effect of EG mass fraction (0.5–20 wt%) on heat storage property was also investigated extensively.

2. Experimental details

2.1. Material preparation

2.1.1. Preparation of EG

EG was obtained from an expandable graphite flake (purity of 99%, 50–60 mesh, from Qingdao Ha Da Co. Ltd., China) by a two-step method. The first step was the preparation of graphite intercalation compounds (GIC). Raw expandable graphite was immersed into concentrated sulfuric acid (H_2SO_4 , 95–98%) and mixed sufficiently, and potassium permanganate (KMnO_4) was added as an oxidizing agent and stirred 3 min. Subsequently, distilled water was poured into and stirred 30 mins at 70°C . The mixture was filtered and rinsed with distilled water until $\text{pH} \sim 7$. The collected wet GIC was dried in a drying oven. The second step was to expand dry GIC by microwave in a microwave oven. The volumes of the graphite before- and after-expansion were measured experimentally. The expanded volumes of EG were controlled corresponding to various irradiation time.

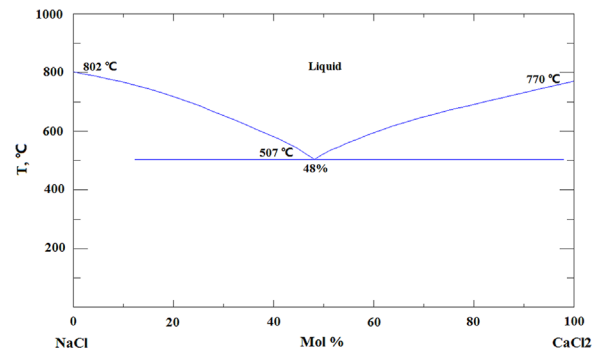


Fig.1. The phase diagram of NaCl-CaCl_2 binary system.

Table 1

Thermophysical properties of NaCl , CaCl_2 and binary eutectic NaCl-CaCl_2 system.

Thermophysical properties	NaCl	CaCl_2	Binary NaCl-CaCl_2 system
Melting temperature (K)	1073.95	1045.00	779.35
Phase change latent heat (J/g)	481.33	257.14	164.20
Specific heat capacity (J/g K)	0.863	0.656	1.243 (330 K)
	(298.15 K)	(298.15 K)	
Thermal conductivity (W/m K) (298.15 K, 2 g/cm ³)	2.039	0.435	0.704

2.1.2. Preparation of binary eutectic chloride

In this study, binary eutectic NaCl-CaCl_2 was selected as PCMs for high temperature heat storage. The phase diagram of NaCl-CaCl_2 binary system [28] was calculated and shown in Fig. 1, and the molar ratio of NaCl:CaCl_2 was 52:48 as a binary eutectic. The thermal-physical properties of sodium chloride, calcium chloride and binary eutectic salt are listed in Table 1. The binary eutectic molten salt was prepared by statically mixing sodium chloride and calcium chloride (AR, $> 99\%$ purity, Sinopharm Chemical Reagent Co., Ltd). Sodium chloride and calcium chloride powder were uniformly mixed firstly, and then the mixture were heated to 600°C and kept for 3 h for a completed fusion.

2.1.3. Preparation of binary eutectic chloride/EG composite

The binary eutectic chloride/EG composites were prepared by impregnation of molten NaCl-CaCl_2 eutectic salt in porous EG at high temperature. First, EG were put into the container with the mass fraction of 0.5–20 wt% and the corresponding binary eutectic chloride were added. Then, the mixtures were heated to 600°C and stirred uniformly. At last, the prepared samples of PCMs were cooled down until fully solidified, as shown in Fig. 2.

2.2. Characterization

2.2.1. Microstructure characterization

The EG and binary eutectic chloride/EG composites morphologies were observed by scanning electron microscopy-energy dispersive spectrometry-electron backscattered diffraction (SEM-EDS-EBSD, model Quanta 400F, FEI/OXFORD/ HKL) at room temperature. The resolution was 2 nm under 30 kV high vacuum.

2.2.2. Specific heat capacity characterization

Specific heat capacity of composites was measured by Sapphire method. Three measurements including blank, sapphire and sample measurement were conducted using a differential scanning calorimeter (DSC, Q600, TA Instrument Inc., USA) analysis. Al_2O_3 crucible was used to hold the sample in the measurement. The sample mass ranged from 5 to 15 mg. A sapphire standard material was used as a reference to perform the specific heat capacity measurements. The standard specific heat capacity data

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