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# Eutectic composition-dependence of latent heat of binary carbonates (Na<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>CO<sub>3</sub>)

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## ABSTRACT

Phase change materials (PCMs) are promising alternative candidates for a variety of thermal energy storage and related applications. Among the PCMs, alkali carbonates have received particular attention in recent years due to their favourable thermophysical properties at high temperatures. However, the use of such carbonates as PCM requires the understanding of the structural information of the material particularly at both the solid and molten states and the composition dependence of the latent heat, which are largely lacking. Here we study, by both experiments and molecular dynamics simulations, the latent heat of the binary carbonates Na<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>CO<sub>3</sub>. The results show that the binary carbonates can convert to LiNaCO<sub>3</sub> within a wide concentration range. A eutectic composition (EC) region of about 51 mol. % Li<sub>2</sub>CO<sub>3</sub> has shown the largest conversion to the LiNaCO<sub>3</sub>. Any excess loading of Na<sub>2</sub>CO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub> beyond the EC region of the carbonates could lower the activation energy of diffusion. The solidification of the carbonates leads to a higher phase change resistance in the EC region with a higher activation energy  $E_a^{(pc)}$  and a larger latent heat during the phase change.

## 1. Introduction

Thermal energy storage (TES) plays an increasingly important role in effective industrial waste heat recovery and sustainable energy production and utilization from intermittent renewable energy sources [1–5]. Among these applications, the TES system often serves as a reservoir to hold and transfer thermal energy by a Heat Transfer Fluid (HTF). Inorganic salts can serve as both a TES material and a HTF, with the most immense potential for applications at high temperatures. Taking binary solar salts (Solar salt, 60/40 wt% of NaNO<sub>2</sub>/KNO<sub>3</sub>) and ternary salt (Hitec, 40/7/53 wt% of NaNO<sub>2</sub>/NaNO<sub>3</sub>/KNO<sub>3</sub>) as examples, they have been widely used in concentrated solar thermal power plants [6–15]. However, the melting point of these salts is high (e.g., ~220 °C for solar salt), leading to the need for auxiliary heating equipment to prevent pipeline freezing and blockage. Furthermore, the decomposition temperature of the salts restricts the use of the salts under ~450 °C. Such a narrow liquid temperature range of the salts are hardly to meet the requirement for a significant TES efficiency [7].

In most concentrated solar thermal power (CSP) plants currently under operation, solar heat is stored in sensible heat form to deal with intermittency. The storage materials are mostly oil based (e.g. Therminol VP1) and a small number of plants use molten salts (e.g. solar salt and Hitec as mentioned above). Due to limited temperature range, the energy density is low, leading to the need for bulky storage

tanks and high costs [16]. The use of salts based solid-liquid phase change materials has the potential to substantially increase the energy density. The use of PCMs also ensures the heat storage and release processes at a nearly constant temperature [17]. Carbonates are among the promising PCM candidates for such applications, not only because such materials have been used in the molten carbonate fuel cell (MCFC) and carbon capture and storage fields [18,19], but also due to their much higher decomposition temperature – one of the key aspects for future high efficiency tower and dish based CSP technologies.

There have been lots of studies on the physical and chemical properties of carbonate salts, such as density, viscosity, and electrical conductivity. There is a lack of a clear insight into the microscopic structure and phase change properties of the carbonates. Here, we focus on the latent heat of carbonate based PCMs, with an aim to elucidate the structure-dependence of latent heat for binary carbonate salt consisting of Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>.

## 2. Experimental and molecular dynamics simulation

## 2.1. Preparation and thermal analysis

Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, Beijing Chemical Works) and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>, Sinopharm Chemical Reagent Co. Ltd) were mixed thoroughly by a preset mole ratio in a crucible. Then, the binary

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carbonate mixture was heated to the melting point (obtained from the phase diagram [20]) and held at the temperature for 0.5 h, followed by naturally cooling down of the sample to the room temperature (ca. 25 °C). The whole process was repeated 4–5 times to ensure uniformity. Simultaneous thermal analyzer (TG-DSC, STA 449 F3 Jupiter®, Germany) was used to study the thermal performance of the samples. The resolution of the calorimeter is 1  $\mu$ W. The onset melting temperature and latent heat of five standard samples (In, Sn, Bi, Zn, and Al) were used for the calibration. The measurements were done under a flow of argon at a flowrate of 10 °C/min. The Kissinger formula was used to determine the apparent activation energy of the binary carbonates during crystallization at the cooling rates of 30, 20, 15, 10 and 5 °C/min.

## 2.2. Structural characterization

The phase and morphological analyses of the mixtures were conducted using an in-situ X-ray diffractometer (XRD, Cu K $\alpha$  radiation, X'Pert PRO MPD, Holland) and a scanning electron microscope (SEM, JSM-7100F, Japan), respectively. During the high-temperature XRD experiments, magnesia powder was used as the reference material and the temperature control procedure was by first heating up to 300–500 °C and then cooling down to 300 °C. Each temperature was held for 30 min for the XRD detection. All the phase identification of XRD analyses were performed with Jade 6 software (MDI, CA) with reference to the standard PDF cards.

## 2.3. Molecular dynamics simulation

Molecular dynamics (MD) simulations were performed by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS; Sandia National Laboratory). The bulk salts (modeled with 6300 molecules) were built with VMD [21]. For interactions between ions, the Electrostatic and Born-type repulsive potential which has been successfully used in the simulation of molten salts was adopted, as shown in Eq. (1).

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + b \left( 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right) \exp[\alpha(\sigma_i + \sigma_j - r_{ij})] \quad (1)$$

where the first term describes the electrostatic interactions and the second term represents Born-type repulsion potential due to overlaps of electron clouds.  $r_{ij}$  is the distance between the centers of the ions,  $z$  is the charge of the ions,  $e$  is the electronic unit charge,  $n$  is the number of outer electrons,  $\sigma$  is the crystal ionic radii,  $\alpha = 3.45 \text{ \AA}^{-1}$  and  $b = 3.38 \times 10^{-20} \text{ J}$  are the softness parameter and pre-exponential term, which determine the steepness and weight of the Born-type interaction, respectively. The parameters for the potential were obtained from the literature [22].

According to the Einstein equation, it is possible to compute the diffusion coefficient,  $D_X$ , of a chemical specie, X, with  $N_X$  numbers from the mean square displacement (MSD) by Eqs. (2) and (3).

$$D_X = \lim_{t \rightarrow \infty} \frac{\langle |\delta r_{X,i}(t)|^2 \rangle}{6t} \quad (2)$$

$$\text{MSD}_X(\tau) = \frac{1}{N_X} \sum_{i=0}^{N_X-1} \langle (r_{X,i}(\tau + t) - r_{X,i}(t))^2 \rangle_t \quad (3)$$

where  $r_{X,i}(t)$  denotes the position of atom  $i$  at time  $t$ . Thus, the diffusion coefficients  $D_X$  can be calculated from the slope of the MSD. The activation energy of diffusion,  $E_a^{(D)}$ , can be obtained by data fitting to the Arrhenius plot given by:

$$\ln(Y) = C - K \frac{E_a^{(D)}}{R} \left( \frac{1}{T} \right) \quad (4)$$

where  $C$  and  $K$  are constants with  $K$  for unit conversion, and  $R$  is the gas constant.

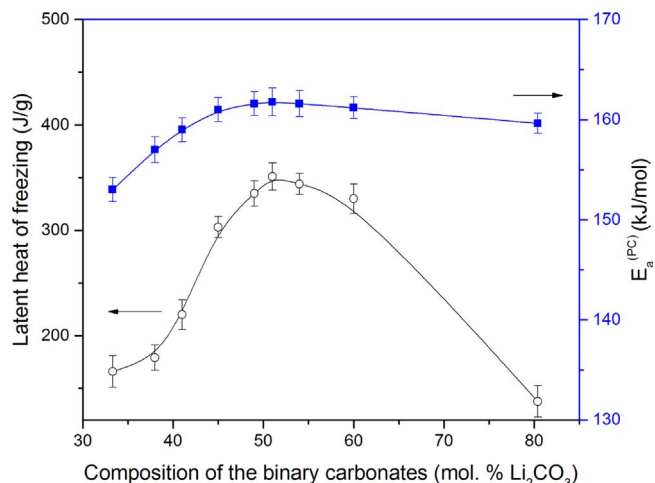


Fig. 1. The values of latent heat obtained from DSC curves at 10 °C/min and the activation energy  $E_a^{(pc)}$  obtained by Kissinger method as a function of the mol. % of  $\text{Li}_2\text{CO}_3$  in the binary mixture.

## 3. Results and discussion

### 3.1. The latent heat

A binary  $\text{Na}_2\text{CO}_3/\text{Li}_2\text{CO}_3$  salt has been reported to have a latent heat of about 330 J/g at the melting point of about 498 °C [23]. In our work, we measured the latent heat of the binary carbonate mixtures with different compositions using the DSC operated at a heating rate of 10 °C/min. Fig. 1 shows the results as a function of the mol. % of  $\text{Li}_2\text{CO}_3$  in the binary mixture. One can find that the latent heat is about 166 J/g for the carbonate mixture with 33 mol. %  $\text{Li}_2\text{CO}_3$  and increases with increasing  $\text{Li}_2\text{CO}_3$  loading until a maximum value of about 351 J/g is achieved at 51 mol. %  $\text{Li}_2\text{CO}_3$ . The latent heat is seen to decrease to 344 J/g at a loading of 54 mol. %  $\text{Li}_2\text{CO}_3$ . A further increase in the molar concentration of  $\text{Li}_2\text{CO}_3$  leads to a considerable reduction of the latent heat to 138 J/g at 80 mol. %  $\text{Li}_2\text{CO}_3$ .

The latent heat was obtained by integrating the area under the DSC curve and this can change with a change in the heating or cooling rate. Fig. 2 shows the DSC curves of the carbonate mixture with 51 mol. %  $\text{Li}_2\text{CO}_3$  during solidification at different cooling rates. From this figure, one can find that, with decreasing heating rate from 30 to 5 °C/min, the peak moves slightly towards to a lower temperature, whereas the latent heat reduces accordingly. Kissinger thought that this variation is only

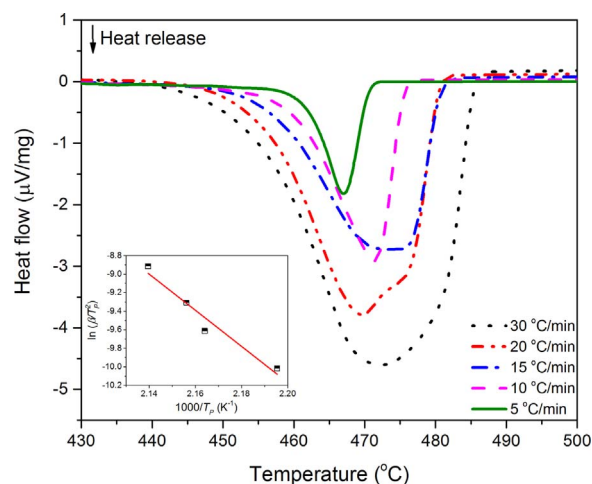


Fig. 2. DSC curves of the carbonate mixture with 51 mol. %  $\text{Li}_2\text{CO}_3$  during solidification at different cooling rates from 30 to 5 °C/min and the Kissinger plot for the activation energy  $E_a^{(pc)}$  as an inset.

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