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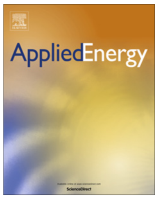

Effects of sodium chloride on the thermal behavior of oxalic acid dihydrate for thermal energy storage

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HIGHLIGHTS

- Oxalic acid dihydrate as a phase change material for TES is studied.
- Thermophysical properties of oxalic acid dihydrate mixtures with NaCl were determined.
- The aim was to improve the cyclic stability of oxalic acid dihydrate.
- The 100 heating and cooling cycles were measured.
- The best sample was oxalic acid dihydrate + 9 wt% NaCl.

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ABSTRACT

Oxalic acid dihydrate (OAD), which is inexpensive and has a high initial phase transition enthalpy, is a very promising phase change material. However, severe material leakage can occur owing to the large amount of steam generated when OAD is heated to melt. This behavior subsequently degrades the thermophysical properties of OAD over time, thereby hindering further application of OAD. In the present study, NaCl was introduced as an additive in OAD to reduce its melting point. Results showed that a NaCl additive content of 9 wt% was the optimal amount to reduce the phase change temperature of OAD and produce sharp endothermal and exothermal peaks without reducing the phase change enthalpy significantly. Furthermore, minimal changes in the thermophysical properties of this mixture were observed after being subjected to 100 thermal cycles. The current findings are expected to broaden the application scope of OAD for thermal energy storage.

1. Introduction

Concerns surrounding the limited availability of fossil fuels to meet increasingly growing energy demands have become more pronounced over the recent years. Accordingly, finding effective solutions to address this issue is essential, however, very challenging. Of the many options considered, the thermal energy storage (TES) technology has attracted great interest in the scientific and industry community. This technology transfers heat to storage media during the charging period, and releases it at a later stage during the discharging step. It can be usefully applied in building energy conservation, air conditioning systems, industrial waste heat recovery, solar energy storage systems and so on [1–4]. The TES technology has great potential as an effective form of energy management to alleviate energy supply issues the world faces [5–9]. Among the various TES techniques, the use of phase change materials (PCMs) is particularly attractive due to their capability of having a high storage density, enabling a compact energy storage system at nearly isothermal conditions and small temperature difference between heat storing and releasing [10–13].

The various PCMs are generally divided into three main categories from the material composition: organic, inorganic and eutectic compounds [14]. Among them, salt hydrates are one of the most promising PCMs, which have been extensively studied for their use in TES systems. The most attractive properties of salt hydrates are their (i) high latent heat of fusion per unit volume, (ii) relatively high thermal conductivity, and (iii) small volume changes upon melting. Moreover, many salt hydrates are inexpensive for use as TES devices [15,16]. Table 1 presents the thermal properties and cost of a few common salt hydrate PCMs. As observed from Table 1, salt hydrates are considerably low-cost PCMs with high heat of fusion. It's worth noting that oxalic acid dihydrate (OAD, $C_2H_2O_4 \cdot 2H_2O$) has a remarkable heat of fusion of

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Table 1
Comparison of thermal properties and cost of a few salt hydrate PCMs for TES.

Material	Wholesale price (USD ton^{-1})[a]	Melting point (°C)	Latent heat (J g^{-1})[b]	Energy storage density/price ratio (kJ USD^{-1})	Ref.
$CH_3COONa·3H_2O$	500–600	58.0	265	442–530	[15]
$Ba(OH)_2·8H_2O$	700–800	78.0	280	350–400	[16]
$Mg(NO_3)_2·6H_2O$	230–250	89.9	167	668–726	[15]
$KAl(SO_4)_2·12H_2O$	300–500	91.0	184	368–613	[15]
$C_2H_2O_4·2H_2O$	500–599	101.0	370	618–740	[17]
$MgCl_2·6H_2O$	90–120	117.0	150	1250–1667	[16]

[a] The wholesale prices of salt hydrates were searched at www.alibaba.com (China).

[b] Products from Alibaba are focused on industrial use, so the properties might be slightly different than those reported for high purity materials at lab scale.

370 J g^{-1}. And its energy storage density/price ratio (618–740 kJ USD^{-1}) is higher than those of most salt hydrate PCMs. Hence, OAD is a very cost-effective and promising PCM for TES. To date, the literature lacks comprehensive studies on the thermal behavior of OAD. Such studies are important to better assess the suitability of OAD and possibly widen its scope of application in TES systems. Accordingly, authors of this paper have considered OAD as the research object.

In OAD molecules, alternating acid and water molecules act both as hydrogen-bond donors and acceptors [18]. OAD requires a considerable amount of energy to break the hydrogen bonds during the melting process, leading to a high phase transition enthalpy. However, the melting point of OAD is 101 °C (onset value), just 1 °C higher than boiling point of water at sea level. When OAD is heated to melt, material leakage can easily occur owing to the high pressure steam generated. Hence, OAD undergoes significant thermophysical property degradations over time. Thus, reducing the melting point of OAD, possibly by preparing eutectic mixtures, would greatly improve the cyclic stability of OAD. However, it is fairly difficult to prepare OAD-based eutectic mixtures because OAD readily forms precipitates with plenty of salt hydrates and has poor miscibility with many organic materials.

Recently, some studies have attempted to accelerate the crystallization of PCMs and reduce their melting point and supercooling degree by introducing salts into the matrix, e.g. sodium chloride (NaCl) [19–22]. It is reported that salt ions dissolved in water may influence the viscosity and entropy of the solution and promote crystalline [23]. Such a phenomenon results from the effect that ions have on the hydrogen-bond network of water molecules [24]. For instance, some ions exhibit weaker interaction with water molecules than internal ions within water molecules, whereas other ions display stronger interactions with water molecules. Such effects influence the degree of supercooling and lead to a lower melting point. In the present study, OAD mixtures containing varying amounts of NaCl were prepared. The effects of NaCl, as an additive, on the thermal properties of OAD including phase change temperature, latent heat, and cyclic stability were systematically investigated. The objective of this work is to optimize the thermal properties of OAD for TES application.

2. Materials and method

Table 2
Samples composition of OAD mixtures with NaCl.

Sample	Composition (% w/w)
I	99% OAD + 1% NaCl
II	97% OAD + 3% NaCl
III	95% OAD + 5% NaCl
IV	93% OAD + 7% NaCl
V	92% OAD + 8% NaCl
VI	91% OAD + 9% NaCl
VII	90% OAD + 10% NaCl

NaCl (99.5%) and OAD (99.5%) were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). All materials were used without further purification. Experiments were carried out according the designed weight rates listed in Table 2. And the mixtures were stirred homogeneously using a magnetic stirrer at 110 °C for 10 min.

The thermal properties of the prepared materials were characterized by differential scanning calorimetry (DSC, Mettler Toledo-DSC2, Switzerland), equipped with a mechanical cooling accessory (Julabo-FT 100, Germany). Temperature calibration was performed using *n*-decane and indium (melting points of −29.66 °C and 156.60 °C, respectively). Heat flow calibration was performed using indium (heat of fusion of 28.45 J g^{-1}). All experiments were performed under nitrogen at a flow rate of 50 mL min^{-1}. Samples of 5–7 mg (±0.0005 mg) were weighed by a microbalance (Mettler Toledo-MS105, Switzerland) and placed onto either aluminum pans or high pressure gold-plated pans (Fig. 1); an empty pan was used as reference. A heating rate of 10 K min^{-1} was used for the measurements.

3. Results and discussion

3.1. Thermal properties of mixtures of OAD and NaCl

DSC measurements of the OAD and NaCl mixtures were initially conducted using aluminum pans. However, an abnormal phenomenon was observed in the DSC curves. For the representative

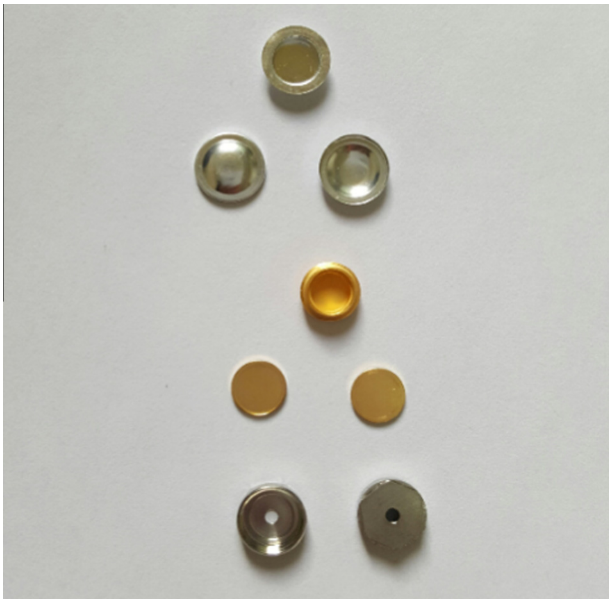

Fig. 1. Appearance of aluminum pan and high pressure gold-plated pan.

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