



# Experimental investigation on copper foam/hydrated salt composite phase change material for thermal energy storage

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## ABSTRACT

Latent thermal energy storage based on hydrated salt as phase change material (PCM) has the potential to store large amounts of energy in relatively small volume. However, the problems of phase separation, high supercooling degree and low thermal conductivity are the common drawbacks for hydrated salts and thus critically limit their energy storage applications. In this study, the hydrated salt of sodium acetate trihydrate (SAT) is firstly modified by using additives with the aim of solving the phase separation and supercooling degree problems, and then the copper foam/hydrated salt composite PCM is prepared by using the modified SAT as PCM and copper foam as supporting matrix to overcome the low thermal conductivity. The thermophysical properties and thermal performance of modified SAT and copper foam/SAT composite PCM are tested and analyzed by using Differential Scanning Calorimeter (DSC), HotDisk Thermal Constant Analyzer and a lab-scale experimental setup. The DSC analysis showed that the modified SAT with the additives of 0.5 wt% carboxyl methyl cellulose (CMC) as the thickener and 2.0 wt% disodium hydrogen phosphate dodecahydrate (DHPD) as the nucleator has the best performance to avoid phase separation. The cycled test revealed that modified SAT has good thermal stability and its supercooling degree is lower than 3 °C. The experimental results showed that the effective thermal conductivity of copper foam/SAT composite PCM is about 11 times higher than that of pure SAT, and its volume heat storage energy density is as high as 467 MJ/m<sup>3</sup>, and this value is 2.2–2.5 times of that of conventional water tank. The results indicated that the copper foam/SAT composite PCM is a promising phase change material for thermal energy storage due to its good thermal stability, low supercooling degree and high thermal conductivity.

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## 1. Introduction

Thermal energy storage has recently become a major focus due to the wide utilization of renewable energy and industrial waste heat recovery. It has the capacity of overcoming the mismatch between energy demand and supply and thus can improve the energy utilization efficiency. Therefore, thermal energy storage plays an important role in reducing fossil fuel consumption and protecting the environment. In recent years, the preparation and application of high-performance composite materials for thermal energy storage have been widely discussed and researched in various renewable energy systems. Phase change material (PCM) is one of the most important and promising thermal energy storage materials because of its high thermal storage density and isothermal operating characteristics [1–3]. The different PCMs mainly

include organic compounds such as paraffin and fatty acids, inorganic substance such as molten salt and hydrated salt, and high-molecular polymer such as polyethylene glycol. The relative researches were focused on the encapsulation, stable form, heat transfer characteristic, thermal properties and applications of different PCMs [4–7]. Among these different PCMs, the inorganic hydrated salt has received widespread concern as a kind of low and medium temperature PCM because it has higher latent heat density and thermal conductivity than that of organic PCM. It is also inexpensive and easy to obtain in the market [8].

The inorganic hydrated salt of sodium acetate trihydrate (SAT) has many advantages of relatively high latent heat of fusion, non-toxic, low price and wide source [9]. SAT is a promising low and medium temperature phase change thermal storage material for domestic hot water storage and building heating. However, SAT suffers the serious phase separation and supercooling problem during energy storage process like most hydrated salts, and thus it needs to add thickener and nucleating agent to improve thermal stability [10]. Dannemand et al. [11] carried out two heat storage

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units based on the principle of stable supercooling of SAT mixtures. One is the pure SAT with 9% extra water to avoid phase separation and the other is the SAT mixture with 1% thickener of carboxyl methyl cellulose (CMC). They found the SAT mixtures are stable and supercooled at indoor ambient temperatures for up to two months. Mao et al. [12] selected five common nucleating agents and three thickeners to improve the thermal stability of SAT. The results indicated that the addition of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and CMC or gelatin as effective additives can reduce the supercooling degree of SAT. Cabeza et al. [13] showed that SAT can be successfully thickened with bentonite and starch additives, and the SAT mixtures has a similar thermal behavior as the pure hydrated salt with the same melting point and its enthalpy decreases between 20% and 35% depending on the type and amount of thickening material used.

Low thermal conductivity of phase change material is another common drawback and it limits the heat exchange capacity during charging and discharging processes [14]. Thus, the heat transfer enhancement of latent heat thermal energy storage system is always a key issue in order to improve the thermal conductivity of PCM. The common method is to develop composite PCM by adding high thermal conductivity additives, such as copper particles, porous metal matrixes such as aluminum foams, and nanometer carbon materials such as nanotubes and graphite. Li et al. [15] studied the effects of different carbon materials (nanotubes, graphene and expanded graphite) on the heat transfer of stearic acid (SA), and found that expanded graphite (EG) is the best additive to improve the thermal conductivity of PCM among different carbon materials and the heat storage rate could be significantly improved. Later, a high performance form-stable EG/SA composite PCM was prepared by using “impregnation of liquid PCM into EG matrix and then compressing into stable-shape block”. The thermal conductivity can be increased by 130 times when compared with the pure SA, and it is as high as  $23 \text{ W/(m}\cdot\text{K)}$  [16]. Shin and Park [17] prepared the EG/SAT composite PCMs using different EG and CMC contents. They confirmed that the thermal conductivity of EG/SAT composite increases with increasing the EG and CMC contents, and it is about  $1.85 \text{ W/(m}\cdot\text{K)}$  as the EG/SAT composite contains 2.5 wt% EG and 5 wt% CMC. 1. Dannemand et al. [18] investigated the thermal conductivity of SAT by adding thickening agents and graphite flakes. They found that the SAT with at least 5% CMC or 1% xanthan rubber can keep graphite powder or graphite flakes to suspend on top of the mixture. However, the hydrophobicity of EG leads to its poor compatibility with hydrated salts, and this means extra additives are required to overcome the hydrophobicity problem at the cost of further decrease in overall phase change enthalpy of composite PCM to a certain extent.

Metal foam as a popular porous material has been widely studied and used to enhance heat transfer performance because of its high specific strength and stiffness, low bulk density, large specific surface areas and especially high thermal conductivity for continuous skeleton structure. It is a feasible method for improving the effective thermal conductivity of organic compounds as PCMs by filling pure PCM powders into the metal foam skeleton [19]. Chen et al. [20] analyzed the heat storage process of solar flat plate collector filled with pure paraffin and aluminum foam/paraffin composite PCM, and found that aluminum foam could improve the heat transfer performance and the temperature distribution is more uniform. Wang et al. [21] compared the phase change processes of pure paraffin and copper/paraffin composite materials using numerical simulations. The results showed that copper foam could effectively improve the internal heat transfer uniformity of paraffin, reduce the heat storage time of paraffin wax by 40%, and improve the relationship between the total phase transition time and the heating boundary temperature. Zhang et al. [22] used copper foam to enhance the thermal conductivity of paraffin and

investigated the phase change heat transfer characteristics of the composite PCM. The results showed that there is a quite large temperature difference between the paraffin and ligament of copper foam due to the thermal non-equilibrium effect in heat transfer between two phases. Zhao et al. [23] performed a numerical study on the solid–liquid phase change in open-cell metal foams using the phase field method by considering the natural convection and the heat transfer between metal foam and PCM, respectively. The results proved that heat conduction through the ligament of metal foams plays a dominant role in the solid–liquid phase change process and the kinetic undercooling effect can be weakened as kinetic coefficient decreases. Cabeza et al. [24] analyzed the corrosion resistance of metal-salt hydrate pairs used for latent heat storage, and they found SAT has a slight corrosion when it contacts with copper and the corrosion weight loss is about  $33 \text{ mg/cm}^2 \text{ yr}$ . However, the aqueous SAT solution have been reported non corrosive on copper alloys at the temperature below boiling point.

The most researches about the inorganic PCMs have been focused on the phase separation and supercooling problems of hydrated salts, and few researches were related to the enhancement of thermal conductivity of inorganic PCM and its thermal performance. In the present study, a new copper foam/hydrated salt composite PCM is prepared by using the modified SAT as inorganic PCM and copper foam as supporting matrix for thermal energy storage. Firstly, the hydrated salt of sodium acetate trihydrate (SAT) is modified by using disodium hydrogen phosphate dodecahydrate (DHPD) as the nucleator and carboxyl methyl cellulose (CMC) as the thickening agent to solve the phase separation and supercooling degree problems of SAT. The optimization contents of DHPD and CMC additives are analyzed and the thermal properties of modified SAT are tested. Secondly, copper foam/SAT composite PCM is prepared by using copper foam as reinforcement material and modified SAT as PCM. The thermal conductivity and thermal stability of the composite materials are measured and discussed. Finally, a small-scale experimental test unit is set up to evaluate the thermal performance of the copper foam/SAT composite PCM, and its charging and discharging performance are investigated experimentally.

## 2. Experiments

### 2.1. Preparation of modified SAT for thermal energy storage

Sodium acetate trihydrate (SAT,  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) is selected as thermal energy storage phase change material for domestic hot water storage and building heating. However, the pure SAT is unsuitable to use as PCM directly because of its supercooling problem. The disodium hydrogen phosphate dodecahydrate (DHPD,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) from Sinopharm Chemical Reagent Corporation and the Carboxyl methyl cellulose (CMC) from Aladdin Industrial Corporation are used as the nucleating agent and thickening agent respectively in order to solve phase separation and supercooling problem during energy storage process. The thermophysical property of different materials used for the modified SAT is measured by using experimental setup and the specifications are shown in Table 1.

The SAT samples are modified by using DHPD and CMC and the modified SAT are prepared using a simple melting-blending method. Firstly, SAT and DHPD nucleator are well mixed at room temperature and then put the SAT mixture into a sealed glass bottle. Afterwards, the glass bottle filled with the mixture is placed in a constant-temperature hot water bath and heated at  $80^\circ\text{C}$  until the PCMs inside bottle are completely melted. Secondly, the CMC thickening agents are added into the liquid mixture inside the glass

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