Article

Development of a New Modified $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ Composite Phase Change Material

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Abstract: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is selected as the original substrate for research, and a new composite phase change material (CPCM) suitable for air-conditioning was developed through experiments. The new modified $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ CPCM uses glycerol as a temperature regulator and barium hydroxide octahydrate as a nucleating agent. The experimental results show that when the mass ratio of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to glycerol is 85:15, the melting temperature of the CPCM is 11.8 °C and the enthalpy of phase change is 112.86 J/g. The chemical composition of the CPCM was characterized by Fourier transform infrared spectroscopy, which confirmed that the material was successfully developed. When the amount of barium hydroxide octahydrate nucleating agent was 1.0 wt.%, the supercooling of the CPCM decreased to 1.22 °C. CPCM still show good stability after 50 thermal cycles and can be used in practical production.

Keywords: calcium chloride hexahydrate; glycerol; barium hydroxide octahydrate; cold storage

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1. Introduction

With the rapid development of society, people's energy consumption is increasing day by day. Air-conditioning power consumption accounts for more than 50% of daily power consumption [1], thus it is very necessary to use a suitable method to reduce the power consumption of air-conditioners. Phase change materials (PCM) can use the valley point of electric power to store energy and release it at the peak point. Therefore, the application of PCM in the field of air-conditioning is one of the hot spots at present. The energy storage technology of PCMs can effectively balance the pressure of the power grid and reduce energy consumption [2].

On the basis of the classification of phase change temperature, PCM can generally be divided into high-temperature (>250 °C), medium-temperature (100~250 °C), and low-temperature (<100 °C) [3]. Low-temperature PCM are generally used in air-conditioning. A PCM with an appropriate melting temperature and a stable performance can be used in air-conditioning. PCMs commonly used in the territory of low-temperature energy storage are generally divided into two categories: organic PCMs and inorganic PCMs. Commonly used organic PCMs are paraffin wax, caprylic acid, lauric acid, lauryl alcohol, etc. Most organic phase change materials generally have no supercooling or phase separation. However, the disadvantages of organic PCMs, such as low thermal conductivity, high price and low latent heat of the phase change, limit the application range of organic materials [4,5]. For example, the price of glycerol used in this paper is 36¥/500 g. However, the price of calcium chloride hexahydrate is 5.2¥/500 g. The price difference between the two is almost seven times. Commonly used inorganic PCMs are barium hydroxide octahydrate, calcium chloride hexahydrate, sodium acetate trihydrate, sodium sulfate decahydrate, sodium chloride solution, etc. Inorganic PCMs have large thermal conductivity, good economic performance, and large latent heat value. However, inorganic PCMs have large supercooling, phase separation, and easy corrosion container. These defects limit the application range of inorganic materials [6–8]. Some scholars use porous media [9,10] and

bionic structures [11–13] to enhance the heat storage effect and heat transfer characteristics of PCM. Some scholars have studied the coupling of inorganic PCMs and organic PCMs. This new CPCPM has the advantages of both organic and inorganic materials, such as large latent heat value, no obvious phase separation and supercooling [14,15].

Calcium chloride hexahydrate has many advantages, such as a suitable phase transition temperature, high enthalpy value, good economic performance, safety, and non-toxicity. It has great potential in the field of low-temperature energy storage [16,17]. However, calcium chloride hexahydrate, as with most inorganic phase change materials, also has serious problems of subcooling and phase separation. Subcooling refers to the situation that phase change materials do not undergo when materials are cooled to the phase change temperature but the temperature continues to decline, which affects the heat storage performance of PCM [18]. To solve the problem of supercooling of calcium chloride hexahydrate, Carlsson et al. [19] used cesium chloride hexahydrate for the first time to reduce the supercooling. Since cesium chloride hexahydrate and calcium chloride hexahydrate have similar crystal forms, they can effectively reduce the nucleation power required for nucleation. When the addition amount of cesium chloride hexahydrate is 2%, the supercooling and cycle times of composite phase change materials reach ideal. Paris [20] studied the subcooling characteristics of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The results show that the melting point of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ will be reduced by using 1% hydrogen oxygen octahydrate, and it is found that the supercooling of calcium chloride hexahydrate can be reduced to nearly zero by using 3% cesium chloride hexahydrate. Zhang et al. [21] found that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is a heterogeneous molten material. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is hydrolyzed at 29 °C to form calcium chloride tetrahydrate. Next, calcium chloride tetrahydrate is transformed into calcium chloride dihydrate at a higher temperature. After repeated cycles there is obvious phase stratification in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, which affects the performance of the material. For the sake of improving the phase separation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Ji et al. [22] developed a new CPCPM based on calcium chloride hexahydrate PCM. The phase change temperature of the CPCPM is 28.6 °C, and the phase change enthalpy is 169.5 J/g. After 100 thermal cycles, the composite material has good performance. In this study, sodium carboxymethyl cellulose (CMC-Na) was used as the thickener. The phase stratification of CPCPM was improved and can be applied in practice. Liu et al. [23] used EG to improve the thermal conductivity of calcium chloride hexahydrate. The thermal conductivity of the modified material is 3.328 W/(m · K), and the subcooling is kept within 2 °C. Calcium chloride hexahydrate can be used in room temperature control, air-conditioning, and cold storage after packaging with microcapsules and porous matrix [24]. Yu et al. [25] use solvent volatilization method to wrap calcium chloride hexahydrate with polymethylmethacrylate as capsule wall material to prepare microcapsule PCM, which can be used in room wall temperature control. Some other scholars used organic materials as temperature regulators to prepare a new type of organic-inorganic CPCPM [26]. Zou et al. [27] used calcium chloride hexahydrate as the original substrate and urea as the temperature regulator to synthesize a new type CPCPM. The ratio of the material is 80 wt.% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + 15 wt.% urea + 5 wt.% ethanol. The phase change temperature of the new CPCPM is 11.62 °C and the enthalpy of phase change is 127.2 J/g, which can be applied to the air-conditioning. However, the phase separation of this material was serious, and thickener needs to be added. Zou et al. [28] further used expanded graphite (EG) to improve the thermal conductivity of the CPCPM. The results show that when EG-50 was used the thermal conductivity of the material is 3.283 W/(m·K), and the subcooling of the CPCPM is further reduced.

In this study, a novel CPCPM based on $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was developed for air-conditioning cold storage system. In the field of air-conditioning, the melting temperature of PCM should be in the range of 5–12 °C [29]. To make the phase change temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ appropriate for air-conditioning, glycerol was used as an additive to modify PCM. Due to the viscosity of glycerol, the synthesized CPCPM has no phase separation and does not need to add thickener. Glycerin was used not only as a temperature regulator but also as a

thickener to modify calcium chloride hexahydrate. The material is simple in composition, convenient in equipment, and can be used in practical production.

2. Materials and Methods

2.1. Materials

In order to ensure the accuracy and consistency of the experiment, calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, AR), glycerol ($\text{C}_3\text{H}_8\text{O}_3$, AR), barium carbonate (BaCO_3 , AR), barium hydroxide octahydrate ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, AR), and sodium chloride (NaCl , AR) used in the experiment were all from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Equipment

DSC-300C (Shanghai Jiezhun, Shanghai, China) was used to test the enthalpy value of CPCM. Before the test, the instrument was calibrated with Tin standard. During the experiment, an empty sealed alumina crucible was used as a reference, and the sample temperature changes in the range of -35 – 50 °C with the heating/cooling rate of 5 °C/min. Nitrogen was used as a protective gas in the experiment. The phase change temperature (T_m) of PCM was determined by drawing a line at the point of maximum slope of the leading edge of the peak and extrapolating to the baseline [27]. The numerical integration of the peak area is the latent heat value. To ensure the accuracy of the experimental data, each sample would be measured three times.

Supercooling was a common phenomenon in inorganic hydrated salt PCM. In order to test and improve the supercooling characteristics of composites, a step cooling experimental platform was built. The main instruments used in the experimental platform are as follows: T-type thermocouple was used to measure the material temperature (accuracy ± 0.1 °C), Agilent 34970A data acquisition instrument (accuracy ± 0.1 °C) was used to record the material temperature change data, one ten thousandth electronic balance was used to weigh the quality of PCM, and low-temperature incubator was used to control the ambient temperature of materials (temperature control range -40 – 150 °C). The diagram of supercooling test platform is shown in Figure 1.

Figure 1. Step cooling experimental platform.

The chemical composition of the material was analyzed by Nicolet is 10 Fourier transform infrared spectrometer of Thermo Fisher company at room temperature. KBr tablet pressing method was used in the experiment, and the scanning range of the instrument was set to 500–4000 cm^{-1} .

3. Result and Discussion

3.1. Development of CPCM

Based on the principle of good economic performance, innocuity, and easy availability, calcium chloride hexahydrate was selected as the main cold storage agent, and glycerol was selected as a temperature regulator. Due to the high viscosity of pure glycerol, the crystal growth was affected. Therefore, the addition amount of glycerol should not be too much. The upper limit of the mass ratio of glycerol in the experiment was set to 20 wt.%. When the amount of glycerol was too small, the melting temperature of the CPCM was not suitable for the field of air-conditioning, therefore, the lower limit of the mass ratio of glycerol in the test was 15 wt.%. The experiment was carried out with materials of different proportions. The mass proportions and serial numbers of mixed reagents in the experiment process are shown in Table 1.

Table 1. Composition of binary mixed sample by mass ratio.

Number	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\text{wt.}\%$	$\text{C}_3\text{H}_8\text{O}_3/\text{wt.}\%$
No.1	85	15
No.2	84	16
No.3	83	17
No.4	82	18
No.5	81	19
No.6	80	20

Stir the reagents in each group with a constant temperature magnetic stirrer for 10 min, and set the temperature at 30 °C when stirring. Seal the reagents with plastic wrap and let them stand until there are no bubbles in the reagents. Suck 20 mg of reagents to the aluminum crucible with a capillary vacuum dropper, place it in DSC to measure the melting temperature and enthalpy of the materials. The obtained data of melting temperature and enthalpy value of each reagent are shown in Table 2.

Table 2. Parameters of melting temperature and enthalpy value of CPCM with different glycerol content.

Additives Content	$\text{C}_3\text{H}_8\text{O}_3$ Content (wt.%)					
	15% (No.1)	16% (No.2)	17% (No.3)	18% (No.4)	19% (No.5)	20% (No.6)
T_m (°C)	11.8	12.2	14.6	12.5	9.2	88.4
ΔH (J/g)	112.86	116.78	103.56	109.07	102.38	84.18

When the additions of glycerol were 15, 16, 17, 18, 19, and 20 wt.%, the phase transition temperatures of the CPCMs were 11.8, 12.2, 14.6, 12.5, 9.2, and 8.4 °C, respectively. No.1, No.5, and No.6 materials, which phase transition temperatures are between 8–12 °C, are suitable for air-conditioning [30]. Therefore, glycerol had a temperature regulating effect on calcium chloride hexahydrate, mainly due to the hydroxyl group in glycerol, which is a hydrophilic group, reacted with the crystal water in calcium chloride hexahydrate, weakening the acting force between CaCl_2 and the crystal water, thus lowering the melting temperature of calcium chloride hexahydrate. Figure 2 is the DSC curve of six groups of materials. It could be seen that the melting temperature (11.8 °C) and phase change

enthalpy (112.86 J/g) were suitable for practical application when the amount of glycerol is 15 wt.%.

Figure 2. DSC curves of each sample.

3.2. Improvement of Subcooling

Inorganic hydrated salt materials generally have the problem of subcooling. Subcooling greatly affects the energy storage performance of phase change materials. There are commonly seven methods to reduce subcooling: (1) Nucleating agent method: select the appropriate nucleating agent according to the principle of heterogeneous nucleation. “Scientific method” and “Edison method” are generally used when selecting nucleating agents. (2) Impurity method: impurities have a great influence on the phase transition of phase change materials. Impurities can promote the heterogeneous nucleation of phase change materials and reduce the subcooling of phase change materials. (3) Cold finger method: retain part of the phase change materials without a phase change in the phase change materials and use the phase change materials without phase change as nucleating agent to reduce the subcooling of the phase change materials. (4) Ultrasonic method: use the high-frequency vibration emitted by ultrasonic to promote the nucleation of materials. High frequency vibration of ultrasonic energy and local high temperature can increase the solubility of phase change materials, effectively improve the phase separation phenomenon of phase change materials, and enhance the heat storage and release performance of phase change materials. (5) Elastic potential energy method: the elastic metal sheet is embedded in the phase change material. The elastic fluctuation produced by elastic metal sheet can induce the crystallization of phase change material to reduce subcooling. (6) Stirring method: the subcooling degree of phase change materials can be effectively reduced by stirring the subcooled phase change materials slowly with a stirring rod. (7) Microcapsule wrapping and porous matrix wrapping method: nano microcapsules or porous matrix are used to wrap the phase change materials, which provides a large nucleation point for the phase

change materials and reduces the subcooling of the phase change materials. Among the above methods, the most common method is to use a nucleating agent. The nucleating agent method has the advantages of a convenient operation, good practical performance, and the obvious effect of reducing undercooling. Therefore, the nucleating agent method is selected in this paper.

At present, the commonly used method is to add a nucleating agent, which can effectively reduce the subcooling degree. Luo et al. [31] used barium carbonate as a nucleating agent to effectively reduce the subcooling of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ to less than 1°C . The selection of nucleating agent should be based on the following two principles: (1) the nucleating agent does not react with the original substrate; (2) the phase transition temperature of a nucleating agent should be higher than that of the original substrate to avoid polluting the original substrate and affecting the heat storage and release performance. After consulting the literature, it was found that barium salt can effectively reduce the subcooling of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and improve the cycle stability of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ system [32]. Therefore, in this study sodium chloride, barium carbonate, and $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ were selected as nucleating agents to observe the influence of each nucleating agent on the supercooling of CPCM. In the experiment, four portions of modified $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ CPCM were weighed, each portion was 20 g, and 0.2 g (1% of the mass fraction of the original substrate) of each nucleating agent was added into the composite phase change material. A plastic wrap was used to seal and a T-thermocouple was inserted to measure the supercooling degree of the material. The measured step cooling curve was shown in Figure 3.

Figure 3. Effects of different nucleating agents on subcooling of composite phase change materials.

From Figure 3, it can be seen that the supercooling of the CPCM without nucleating agent is 4.64°C , and that of the CPCM with NaCl as nucleating agent is 5.68°C . Sodium chloride had no improvement on the supercooling of the CPCM, so it cannot be used as a nucleating agent. The supercooling degree of the CPCM with barium carbonate as the nucleating agent was 0.2°C , but its latent heat platform fluctuated greatly, which affected the heat storage and release stability of the CPCM, therefore, it was not recommended to

be used as a nucleating agent. The subcooling of the CPCM with barium hydroxide octahydrate as a nucleating agent was $1.2\text{ }^{\circ}\text{C}$, and the addition of barium hydroxide octahydrate promoted the heat release of the CPCM system, thus barium hydroxide octahydrate should be used as a nucleating agent.

Barium hydroxide octahydrate was used as a nucleating agent. Barium hydroxide octahydrate with a mass fraction of 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% was added into a certain amount of CPCMs, respectively. The measured step cooling curve was shown in Figure 4.

Figure 4. Effect of different addition amounts of barium hydroxide octahydrate nucleating agent on supercooling of CPCM.

Figure 4 shows that with the increase of a nucleating agent addition, the subcooling of the CPCM system first increases and then decreases. The supercooling of the CPCM system can be reduced to the minimum when the amount of nucleating agent was 1.0 wt.%, thus when barium hydroxide octahydrate was used as a nucleating agent, the recommended amount was 1.0 wt.%.

3.3. FTIR Analysis

Glycerol, calcium chloride hexahydrate, and CPCM were analyzed by Fourier transform infrared spectrometer, and the analysis results are shown in Figure 5. The FTIR spectra in Figure 5 are CPCM, glycerol, and calcium chloride hexahydrate from top to bottom. In the spectrum of glycerol, the infrared absorption peak at the frequency of 3328 cm^{-1} belongs to the stretching vibration of $-\text{OH}$. The infrared absorption peak at 2938 cm^{-1} frequency belongs to the asymmetric stretching vibration of CH_2 . The infrared absorption peak at 2883 cm^{-1} frequency belongs to the symmetric stretching vibration of CH_2 . The infrared absorption peak at the frequency of 1415 cm^{-1} belongs to the bending vibration of CH_2 . The infrared absorption peak at 1110 cm^{-1} frequency belongs to the asymmetric stretching vibration of $\text{C}-\text{O}$. The infrared absorption peaks at frequencies of 1042 cm^{-1} and

993 cm^{-1} belong to the symmetric contraction vibration of C-O. In the spectrum of calcium chloride hexahydrate, the absorption peak from 3300 cm^{-1} to 3600 cm^{-1} was the stretching vibration of crystal water -OH in calcium chloride hexahydrate. The absorption peak at 2163 cm^{-1} was the characteristic band of CaCl_2 . The frequency of 1630 cm^{-1} was the bending vibration of H-O-H of crystal water; 547 cm^{-1} was the H-O-H rotation movement of crystal water. As can be seen from Figure 5, the characteristic peaks of calcium chloride hexahydrate and glycerol all appear in the CPCM, which indicates that the CPCM has been successfully prepared. There is no new characteristic peak in the spectrum of the CPCM, which shows that the components are only physical-mechanical coupling, and there is no chemical reaction.

Figure 5. FTIR spectra of CPCM, glycerol and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

3.4. Thermal Reliability

Thermal stability test is an important test for CPCM performance. After multiple thermal cycles, the enthalpy value of most inorganic hydrated salt CPCM will decrease, the supercooling will increase and obvious phase separation will appear.

Phase separation generally occurs in the phase transformation process of $\text{AB} \cdot x\text{H}_2\text{O}$ type inorganic hydrated salt phase change materials. $\text{AB} \cdot x\text{H}_2\text{O}$ inorganic hydrated salt converted to $\text{AB} \cdot y\text{H}_2\text{O}$ inorganic hydrated salt and a certain amount of H_2O . The phase transformation mechanism is $\text{AB} \cdot x\text{H}_2\text{O} \rightleftharpoons \text{AB} \cdot y\text{H}_2\text{O} + (x - y)\text{H}_2\text{O}$. After the phase change materials with poor solubility are melted, part of the salt is in an insoluble state, and the insoluble salt precipitates at the bottom of the container due to its high density. With the increase of thermal cycles, phase stratification seriously hinders the heat storage capacity of phase change materials. After a certain thermal cycle, the thermal storage capacity of PCM is completely lost. The following four methods are commonly used to solve the phase stratification of phase change materials: (1) Thickener method: the thickener method uses the thickener to increase the viscosity of the phase change

material. After the viscosity of the phase change material increases, the solid particles in the liquid can be evenly distributed in the solution without depositing at the bottom, which can effectively alleviate the phase stratification of the phase change material. (2) Nano microcapsule wrapping method: nano microcapsules are used to wrap phase change materials. Due to the small internal space of nano microcapsules, inorganic hydrated salt phase change materials are difficult to precipitate, which can solve the problem of phase separation of phase change materials. (3) Ultrasonic vibration method: a large number of cavitation bubbles are generated by ultrasonic vibration at high frequency. The cavitation bubbles produce a local high temperature, which can increase the solubility of phase change materials and fundamentally solve the phenomenon of phase stratification. (4) Stirring method: stir the phase change material during the phase change process to reduce the phase separation of the phase change material. Since the thickener has a wide range of sources and convenient operation, the thickener method has a wide range of application. Most scholars use thickeners to increase the viscosity of the material and reduce the phase separation of the material.

In this study, glycerol was used as a temperature regulator. Moreover, glycerol is viscous and can be used as a thickener. It is found that there is no phase separation in the modified $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ CPCM, and there is no need to add thickener. The actual picture of the experiment is shown in Figure 6.

Figure 6. Experimental diagram of phase stratification.

The step cooling curve of the new modified calcium chloride hexahydrate CPCM after 50 thermal cycles was shown in Figure 7.

It can be clearly seen from Figure 7 that the subcooling of the new CPCM only increased by 0.28°C after 50 cycles, and the subcooling of the CPCM did not increase obviously with the increase of cycles. Samples of the CPCM after each cycle were taken for DSC test, the change of melting temperature and enthalpy was observed. The experimental results are shown in Figure 8.

By sorting out the enthalpy values and phase change temperature data of each sample in Figure 8 into Table 3, it can be seen that the melting temperatures of the CPCM are 11.7 , 10.3 , 11.9 , 11.3 , and 11.8°C , respectively, and the corresponding enthalpy values are 111.33 , 119.72 , 119.39 , 115.43 , and 111.48 J/g , respectively. The results showed that the thermal properties of the CPCM remained almost unchanged after many thermal cycles.

Figure 7. Cooling curves of CPCMs at different cycle numbers.

Figure 8. DSC curves of CPCMs under different cycles.

Table 3. Phase change temperature and enthalpy of CPCMs under different cycles.

No. of Cycles	10	20	30	40	50
$T_m(^{\circ}\text{C})$	11.7	10.3	11.9	11.3	11.8
$\Delta H (\text{J/g})$	111.33	119.72	119.39	115.43	111.48

4. Conclusions

In this paper, a new type of phase change energy storage material was developed. This new type of phase change energy storage material uses calcium chloride hexahydrate as the original substrate and glycerol as the temperature regulator. Different proportions are used in the experiment. The experiment draws the following conclusions:

1. After DSC test, it was found that when the mass ratio of calcium chloride hexahydrate to glycerol was 85:15, the phase change temperature of the composite phase change material was 11.8 °C and the enthalpy of phase change was 112.86 J/g, which was suitable for the field of air-conditioning.
2. FTIR confirmed that the material was successfully developed and proved that the two reagents only acted physically, without chemical reaction.
3. The material still showed good thermal stability after 50 thermal cycles. The subcooling of the new CPCM only increased by 0.28 °C after 50 cycles and the enthalpy of CPCM has almost no change.

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References

1. Li, J.; Li, Z.; Yang, S.; Tao, H.; Yao, H.; Wu, C. Application of Dueling-DQN in air conditioning energy saving control. *Comput. Syst. Appl.* **2021**, *30*, 271–279.
2. Navidbakhsh, M.; Shirazi, A.; Sanaye, S. Four E analysis and multi-objective optimization of an ice storage system incorporating PCM as the partial cold storage for air-conditioning applications. *Appl. Therm. Eng.* **2013**, *58*, 30–41. [\[CrossRef\]](#)
3. Nagano, K.; Ogawa, K.; Mochida, T.; Hayashi, K.; Ogoshi, H. Thermal characteristics of magnesium nitrate hexahydrate and magnesium chloride hexahydrate mixture as a phase change material for effective utilization of urban waste heat. *Appl. Therm. Eng.* **2004**, *24*, 221–232. [\[CrossRef\]](#)
4. Cunha, J. Thermal energy storage for low and medium temperature applications using phase change materials-A review. *Appl. Energy* **2016**, *177*, 227–238. [\[CrossRef\]](#)
5. Sar, A. Eutectic mixtures of some fatty acids for latent heat storage: Thermal properties and thermal reliability with respect to thermal cycling. *Energy Convers. Manag.* **2006**, *47*, 1207–1221. [\[CrossRef\]](#)
6. Luo, X.; Zhang, X.; Hou, X.; Hua, W.; Han, X.; Li, J. Experimental Analysis on Heat Release of Pulsating Heat Pipe Phase Change Heat Accumulator With Anhydrous Ethanol. *J. Eng. Thermophys.* **2018**, *39*, 1524–1531.
7. Han, B.; Choi, J.; Dantzig, J.; Bischof, J. A quantitative analysis on latent heat of an aqueous binary mixture. *Cryobiology* **2006**, *52*, 146–151. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Oro, E.; Miro, L.; Barreneche, C.; Martorell, I.; Farid, M.; Cabeza, L. Corrosion of metal and polymer containers for use in PCM cold storage. *Appl. Energy* **2013**, *109*, 449–453. [\[CrossRef\]](#)
9. Shi, T.; Xu, H.; Qi, C.; Lei, B.; Wu, Y.; Zhao, C. Multi-physics modeling of thermochemical heat storage with enhance heat transfer. *Appl. Therm. Eng.* **2021**, *198*, 117508. [\[CrossRef\]](#)
10. Xu, H.; Wang, Y.; Han, X. Analytical considerations of thermal storage and interface evolution of a PCM with/without porous media. *Int. J. Numer. Methods Heat Fluid Flow* **2019**, *30*, 373–400. [\[CrossRef\]](#)

11. Dong, Y.; Wang, F.; Yang, L.; Shi, X.; Zhang, G.; Shuai, Y. Thermal Performance Analysis of PCM Capsules Packed-Bed System with Biomimetic Leaf Hierarchical Porous Structure. *J. Therm. Sci.* **2021**, *30*, 1559–1571. [\[CrossRef\]](#)
12. Dong, Y.; Wang, F.; Zhang, Y.; Shi, X.; Zhang, A.; Shuai, Y. Experimental and numerical study on flow characteristic and thermal performance of macro-capsules phase change material with biomimetic oval structure. *Energy* **2022**, *238*, 121830. [\[CrossRef\]](#)
13. Wang, F.; Dong, Y.; Li, Y.; Xu, J.; Zhang, G. Numerical study on the thermal performance of packed-bed latent heat thermal energy storage system with biomimetic alveoli structure capsule. *Sci. China Technol. Sci.* **2021**, *64*, 1544–1554. [\[CrossRef\]](#)
14. Ying, Y.; Shen, H. Investigation on Cryogenics Cool Thermal Energy Storage Phase Change Composition Material. *J. Low Temp. Phys.* **2009**, *31*, 144–147.
15. Li, J.; Xie, R.; Liu, G. Development of New Low-temperature Phase Change Material and Equipment Used in Refrigerated Transportation. *J. Refrig.* **2018**, *39*, 32–37.
16. Kenisarin, M.; Mahkamov, K. Salt hydrates as latent heat storage materials: Thermophysical properties and costs. *Solar Energy Mater. Sol. Cells* **2016**, *145*, 255–286. [\[CrossRef\]](#)
17. Zhang, X.; Zhou, Y.; Li, X.; Shen, Y.; Hai, C.; Dong, O.; Ren, X.; Zeng, J.; Sun, Y.; Wang, S.; et al. Research progress of inorganic hydrated salt phase change energy storage materials based on calcium chloride hexahydrate. *Energy Storage Sci. Technol.* **2018**, *7*, 40–47.
18. Zhang, X.; Zhou, S.; Liu, S.; Li, Y.; Xu, X. Cold Storage Characteristics of n-Octanoic-Lauric Acid Nanocomposite Phase Change Material. *J. Tianjin Univ. Sci. Technol.* **2019**, *52*, 71–77.
19. Carlsson, B.; Szymne, H.; Wettermark, G. An incongruent heat-of-fusion system-CaCl₂·6H₂O- Made congruent through modification of the chemical composition of the system. *Sol. Energy* **1979**, *23*, 343–350. [\[CrossRef\]](#)
20. Paris, J.; Jolly, R. Observations sur le comportement a la fusion-solidification du chlorure de calcium hexahydrate. *Thermochim. Acta* **1989**, *152*, 271–278. [\[CrossRef\]](#)
21. Zhang, X.; Zeng, T.; Chen, Y. Development of improved calcium chloride hexahydrate phase change cold storage material. In Proceedings of the 13th Yangtze River Delta Energy Forum, Hangzhou, China, 1 October 2016; pp. 251–256.
22. Ji, J.; Zeng, T.; Zhang, X.; Gao, Y.; Chen, Y. Preparation and properties of calcium chloride hexahydrate phase change material after modified. *Cryog. Supercond.* **2017**, *45*, 71–76.
23. Liu, X.; Wu, J.; Xian, T.; Feng, Y. Preparation and properties of CaCl₂ /expanded graphite composite phase change materials. *J. Zhejiang Univ.* **2019**, *53*, 1291–1297.
24. Bayes-Garcia, L.; Ventola, L.; Cordobilla, R.; Benages, R.; Cuevas-Diarte, M.A. Phase Change Materials (PCM) microcapsules with different shell compositions: Preparation, characterization and thermal stability. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1235–1240. [\[CrossRef\]](#)
25. Yu, J.; Liu, T. Preparation and Characterization of Microencapsulated Phase Change Coating. *Appl. Mech. Mater.* **2012**, *204–208*, 4173–4176. [\[CrossRef\]](#)
26. Fu, W.; Zou, T.; Liang, X. Thermal properties and thermal conductivity enhancement of composite phase change material using sodium acetate trihydrate-urea/expanded graphite for radiant floor heating system. *Appl. Therm. Eng.* **2018**, *138*, 618–626. [\[CrossRef\]](#)
27. Zou, T.; Fu, W.; Liang, X. Preparation and performance of modified calcium chloride hexahydrate composite phase change material for air-conditioning cold storage. *Int. J. Refrig.* **2018**, *95*, 175–181. [\[CrossRef\]](#)
28. Zou, T.; Liang, X.; Wang, S. Effect of expanded graphite size on performances of modified CaCl₂·6H₂O phase change material for cold energy storage. *Microporous Mesoporous Mater.* **2020**, *305*, 110403. [\[CrossRef\]](#)
29. Wang, X.; Dennis, M.; Hou, L. Clathrate hydrate technology for cold storage in air conditioning systems. *Renew. Sustain. Energy Rev.* **2014**, *36*, 34–51. [\[CrossRef\]](#)
30. Gang, L.; Hwang, Y.; Radermacher, R. Review of cold storage materials for air conditioning application—Science Direct. *Int. J. Refrig.* **2012**, *35*, 2053–2077.
31. Luo, X.; Lu, X.; Cao, S.; Zou, C. Analysis on the Improvement of Thermal Performance of Phase Change Material Ba (OH)₂ · 8H₂O. *Energies* **2021**, *14*, 7761. [\[CrossRef\]](#)
32. Liu, D.; Xu, Y. Effect of nucleating agent on thermal storage properties of CaCl₂·6H₂O phase change materials. *J. Sol. Energy* **2007**, *028*, 732–738.