Research Progress on Phase Change Cold Storage Materials: Postprint

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Abstract

Phase change cold storage materials exhibit high energy storage density and possess broad application prospects in efficient energy utilization and energy conservation. This paper classifies phase change cold storage materials with solid-liquid phase transition points below 20 ℃, comprehensively summarizes various types of phase change materials that are currently extensively researched and commercially available along with their thermophysical parameters, and compares the thermophysical and chemical properties of different categories of phase change materials. Finally, this paper provides an outlook on the research and application prospects of phase change cold storage materials.

Full Text

Preamble

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Research Progress on Phase Change Materials for Cold Thermal Energy Storage

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Abstract: Phase change materials for cold storage exhibit high energy storage density and offer broad application prospects in efficient energy utilization and energy conservation. This paper categorizes phase change materials with solid-liquid phase transition points below 20 ℃ and provides a detailed summary of the various types of phase change materials currently under intensive investigation or already commercialized, along with their thermophysical parameters. The thermophysical and chemical properties of different categories of phase change materials are compared. Finally, the research and application prospects of phase change materials for cold storage are discussed.

Keywords: cold thermal energy storage; phase change materials; thermophysical properties; latent heat

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Review of Phase Change Materials for Cold Thermal Energy Storage

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Abstract: Due to high energy density, phase change materials for cold storage have great potential for improving the efficiency of energy utilization and saving energy. This paper defines the categories of phase change materials with solid-liquid phase change points below 20 ℃, which are widely used for cold storage, and reviews their thermophysical properties. In addition, the paper further compares different categories of phase change materials regarding their thermophysical and chemical properties. Finally, the paper discusses the future research and application of phase change materials for cold storage.

Key words: cold thermal energy storage; phase change materials; thermophysical properties; latent heat

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Introduction

Cold thermal energy storage (CTES) is a technology that stores cooling capacity at temperatures below ambient for later use. It serves as a supplement and adjustment to refrigeration technology, providing an economically feasible method to coordinate the temporal and intensity mismatches between cooling supply and demand. To date, CTES has been widely applied in civil and industrial air conditioning [?], refrigerator and cold storage applications [?, ?], refrigerated vehicles [?], and building energy efficiency [?], creating a win-win situation for both power systems and end users. CTES technologies are primarily divided into three categories: sensible heat storage, latent heat storage, and thermochemical storage. Among these, latent heat storage using phase change materials (PCMs) has attracted extensive attention and research due to its energy storage density that is 5-14 times higher than the other two methods [?].

Phase change materials can undergo phase transitions at constant or near-constant temperatures while absorbing or releasing large amounts of thermal energy, meaning they exhibit high effective specific heat within their phase transition temperature range [?]. The heat stored in latent heat storage can be expressed as:

$$\int_{T_1}^{T_{pc}} mc_s dT + m\Delta H_{ls} + \int_{T_{pc}}^{T_2} mc_l dT$$

where T_1, T_{pc}, and T_2 represent the initial temperature, phase change temperature, and final temperature, respectively, in K; m is mass in kg; c_s and c_l are the specific heats of the solid and liquid phases, respectively, in $J \cdot g^{-1} \cdot K^{-1}$; and ΔH_{ls} is the latent heat of phase change in $J \cdot g^{-1}$.

Leveraging the advantages of stable phase transition temperatures and high energy storage density, many researchers have devoted themselves to developing new PCMs and measuring their thermophysical properties such as phase change temperature and latent heat. For instance, Xu et al. [?] prepared a metal-based composite high-temperature phase change material using binary eutectic carbonate (Li_2CO_3-K_2CO_3) as the storage material and copper foam as the matrix, achieving high thermal conductivity and storage density. Differential scanning calorimetry measurements showed a phase change temperature of 486.7 ℃ and latent heat of 326.8 $J \cdot g^{-1}$. Zuo et al. [?] investigated the thermal properties of caprylic acid, lauric acid, and their binary systems using differential scanning calorimetry and low-temperature microscopy, demonstrating that a eutectic forms at higher caprylic acid mass fractions with a melting temperature of 7.44 ℃ and latent heat of 136.43 $J \cdot g^{-1}$. Chen et al. [?] prepared and characterized a dodecane/expanded graphite composite PCM for cold storage, revealing a phase change temperature range of -10.62 to -9.82 ℃ and latent heat of 124.8-125.1 $J \cdot g^{-1}$. Another study [?] employed vacuum impregnation to prepare graphite foam/paraffin composite PCMs, finding that while the phase change temperature remained essentially unchanged compared to pure paraffin, the latent heat decreased by 4% and thermal conductivity increased by 311 times.

However, significant challenges remain in the practical selection and application of PCMs due to the lack of accurate classification and systematic selection criteria. Some scholars have recognized this issue and summarized certain PCMs. Li et al. [?] provided a detailed review and analysis of PCMs with phase change temperatures below 0 ℃, particularly focusing on hydrated salts and eutectic salt solutions. Pereira da Cunha et al. [?] reviewed PCMs with phase change temperatures between 0–250 ℃, finding that hydrated salts and organic PCMs dominate the 0–100 ℃ range, while eutectic PCMs are primarily used in the 100–250 ℃ range. Zhai et al. [?] summarized PCMs used in air conditioning and high-temperature cold storage systems, particularly those with phase change temperatures between 6–15 ℃. Kamali [?] analyzed PCMs for building energy efficiency, which are mainly applied in the 20–27 ℃ temperature range. Cabeza et al. [?] reviewed PCMs for domestic hot water supply (phase change temperature 29–60 ℃) and waste heat recovery (phase change temperature above 120 ℃).

Overall, current research has extensively investigated PCMs with phase change temperatures above 20 ℃. In contrast, PCMs below 20 ℃ still hold vast application potential, yet existing studies have not systematically compiled and analyzed these materials. Therefore, this paper first establishes a systematic classification of cold storage PCMs and elaborates on the advantages and disadvantages of each category. Second, it summarizes PCMs with phase change temperatures below 20 ℃ from both research and commercial perspectives according to this classification. Finally, it compares and analyzes the main thermophysical and chemical properties of different types of cold storage PCMs, providing references for material selection in future research and engineering applications to promote broader application of cold storage PCMs across multiple fields.

1 Classification of Phase Change Materials for Cold Storage

As shown in Figure 1 [Figure 1: see original paper], phase change materials can be divided into four types: solid-solid, solid-gas, liquid-gas, and solid-liquid. However, the first three types are difficult to implement at large scales due to significant pressure changes, small phase change enthalpy, and other drawbacks. In contrast, solid-liquid PCMs generally offer better practicality. Solid-liquid PCMs can be broadly categorized into three major groups: organic materials, inorganic materials, and eutectic materials.

1.2.1 Hydrated Salts

Hydrated salts ($AB \cdot nH_2O$) are crystals formed by the combination of inorganic salts and water. The solid-liquid transition of hydrated salts is essentially a process of water absorption and dehydration, similar to freezing and melting in thermodynamics, with phase change enthalpy depending on the bond strength between water molecules and salt molecules. The dehydration process exhibits incongruent melting, sometimes losing only part of the crystalline water:

$$AB \cdot nH_2O \rightarrow AB \cdot mH_2O + (n-m)H_2O$$

or losing all crystalline water:

$$AB \cdot nH_2O \rightarrow AB + nH_2O$$

Hydrated salts offer advantages including high latent heat, high thermal conductivity, small volume change during phase transition, minimal thermal stress effects, low toxicity, and low cost. However, issues such as supercooling, phase separation, and corrosion with common metals (copper, aluminum, stainless steel) constrain their application in cold storage systems.

To improve the poor nucleation performance of hydrated salts, the commonly adopted solution is to add nucleating agents to provide crystal nuclei. For example, Xu et al. [?] used $CaCl_2 \cdot 6H_2O$ as the base material and demonstrated in an open system at room temperature cooling conditions that adding borax could reduce supercooling to 2 ℃, effectively solving the supercooling problem.

1.2.2 Inorganic Compounds

Inorganic compounds typically refer to compounds without carbon elements, but including carbon oxides, bicarbonates, carbonates, cyanides, etc. Due to their generally small latent heat and the fact that most inorganic compounds are harmful to the environment and human health (e.g., NaOH in Table 2 has strong corrosiveness), they are difficult to apply widely in cold storage systems.

1.2.3 Metal Alloys

Although some low-melting-point metals and their alloys have not been widely applied in cold storage systems due to their high density, they possess advantages such as high latent heat, high thermal conductivity, high electrical conductivity, low vapor pressure, and small volume change during phase transition. Consequently, low-melting-point liquid metals have already played an irreplaceable role in cooling applications for laser systems [?], USB flash drives [?], and mobile phones [?].

1.3 Eutectic Phase Change Materials

Eutectic PCMs are typically crystalline mixtures formed by two or more low-melting-point components during the crystallization process, which can be subdivided into organic eutectic materials and inorganic eutectic materials (primarily eutectic salt solutions). The greatest advantage of eutectic PCMs is the ability to control the phase change temperature by adjusting the proportion of each component. For example, crystallization of tetradecane with octadecane, docosane, and heneicosane can achieve a phase change temperature range of -4 to 5.56 ℃. Additionally, eutectic PCMs offer high thermal conductivity, high density, no phase separation, and no supercooling. However, their latent heat and specific heat are relatively lower compared to alkanes and hydrated salts. Tables 3 and 4 list the widely studied organic and inorganic eutectic PCMs and their thermophysical parameters.

To obtain eutectic PCMs with suitable phase change temperatures and high latent heat, many researchers have experimentally measured the thermophysical parameters of eutectic materials with different component ratios to identify optimal properties. Li [?] investigated a ternary eutectic PCM composed of glycerol, sodium acetate, and water, testing four samples with mass ratios of 2:2:6, 1:2:7, 1:1:8, and 2:1:7. The results showed that the mixture with a sodium acetate:glycerol:water ratio of 1:1:8 exhibited the best thermal properties, with a phase change temperature of -14 ℃ and latent heat of 172 $J \cdot g^{-1}$. Yang et al. [?] experimentally prepared a binary eutectic PCM of caprylic acid and myristyl alcohol, varying the caprylic acid mass fraction from 0% to 75%. They found that stability was optimal at 74% caprylic acid mass fraction, yielding a phase change temperature of 6.9 ℃ and latent heat of 151 $J \cdot g^{-1}$.

1.4 Commercial Phase Change Materials

In addition to PCMs that have received widespread attention in research, many PCMs have matured and entered commercialization. Table 5 provides a categorized summary of PCM products from companies such as Cristopia and Rubitherm GmbH [?, ?]. The data show that commercial cold storage PCMs are primarily eutectic salt solutions and organic alkanes, accounting for 61% and 29% of products respectively, with smaller quantities of fatty acids and hydrated salts. Eutectic salt solutions have become the preferred choice for low- and medium-temperature cold storage systems operating below 0 ℃ due to their phase change temperature controllability through solute concentration adjustment. Organic alkanes, offering chemical stability and low manufacturing costs compared to hydrated salts and fatty acids, have been widely applied in high-temperature cold storage systems operating above 0 ℃.

2 Analysis of Phase Change Materials for Cold Storage

Figure 2 [Figure 2: see original paper] illustrates the relationship between latent heat and phase change temperature for different types of cold storage PCMs. The results indicate that organic materials have phase change temperatures primarily distributed between -10 and 20 ℃, with latent heat ranging from 80 to 280 $J \cdot g^{-1}$. In the -5 to 5 ℃ range, organic materials show particular promise. From both research and commercial perspectives, eutectic salt solutions and organic PCMs are the most widely studied and utilized solid-liquid PCMs for temperatures below and above 0 ℃, respectively.

Despite significant advancements in PCM research for cold storage, several areas warrant further investigation:

First, organic PCMs offer a wide applicable temperature range and exhibit no supercooling or phase separation phenomena, but their thermal conductivity is generally low. Improving thermal conductivity remains a subject for further research. Second, inorganic PCMs possess strong thermal conductivity and storage capacity and are inexpensive and readily available, yet suitable nucleating agents and anti-supercooling additives must be identified to optimize their phase change performance. Third, the phase change temperature of eutectic PCMs can be controlled by adjusting component mass fractions, but methods to enhance latent heat and specific heat require further study. Fourth, research on composite mechanisms and development of novel composite PCMs to overcome the limitations of single-component PCMs could yield better thermal properties and stability. Fifth, current research often focuses only on phase change temperature and latent heat, while other thermophysical parameters such as specific heat, density, and thermal conductivity receive less attention. Establishing a comprehensive PCM thermophysical property database requires precise measurement of these additional parameters to facilitate practical material selection.

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Note: Figure translations are in progress. See original paper for figures.