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COMMENTARY

Toward high-energy-density phase change thermal storage materials

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Phase change materials (PCMs), capable of reversibly storing and releasing tremendous thermal energy during nearly isothermal and isometric phase state transition, have received extensive attention in the fields of energy decarbonization, passive thermal management, etc. Developing pure or composite PCMs with high thermal energy storage density are highly desired for designing compact, cost-effective, and versatile thermal storage devices, but it is also highly challenging. In recent years, new mechanisms and methods for increasing the phase-change thermal storage density are emerging.

MECHANISMS FOR THERMAL ENERGY STORAGE OF PCMS

As basic thermodynamic parameters, the volumetric or gravimetric latent heat, or enthalpy of fusion of PCMs are the main factors to determine the thermal storage density in device and system scales. Enthalpy of fusion of PCM denotes the energy required to overcome inter- and intramolecular interactions in the solid state, which essentially depend on the material type and its thermodynamic state parameters including the temperature (T), pressure (p), etc.[1] From a thermodynamic perspective, a single-component system under two phase equilibrium state has thermodynamic parameters following the Clapayron equation, $dp/dT=\Delta H/(T\cdot\Delta V)$. Among different types of phase transitions, only some first-order phase transitions like solid-liquid transition and partially solid-solid transition have high latent heat (ΔH) and small volume change (ΔV), appropriate for thermal energy storage.

At the micro level, the common molecular interactions within PCMs that contribute to latent heat (energy storage potential) include van der Waals force, hydrogen bonding, metal hydrate bonding, and coulombic interaction (Figure 1A). Some materials are dominated by a single type of interaction, such as inorganic salts (electrostatic), and some experience a combination of two (*e.g.*, inorganic salt hydrates) or even more (*e.g.*, ionic liquids, organic salts, or polymers) types of interaction. For salt hydrates that have a general formula of $AB{\cdot}nH_2O$, the interactions are primarily a combination of hydrogen and ionic bonds. For some organic PCMs like sugar alcohols, carboxylic acids, ionic liquids, organic salts, polymers, etc., van der Waals interactions are enhanced by intermolecular and/or intramolecular hydrogen bonds. Particularly, the short-range interactions like hydrogen bonding have different strengths that depend on their length, angle, and other factors. It should be noted that the multiple interactions have complicated effects on the enthalpy of fusion of PCMs and the strength of the interaction is not the only decisive factor. For example, the most commonly-used organic PCMs, *i.e.*, paraffin wax family, rely solely on intermolecular van der Waals forces with the strength about 10 times weaker than hydrogen bonds, but provides the relatively high enthalpies of fusion, up to 130 kJ mol^{-1}, which is far higher than most salt hydrates with abundant hydrogen bonds (appropriately 40-80 kJ mol^{-1}).[1] Different from the solid-liquid PCMs that utilize the changes in inter- and/or intramolecular interactions, two other ways of storing thermal energy, including the molecular isomerization conversions and chemical reactions, mainly involves intramolecular interactions (Figure 1A).

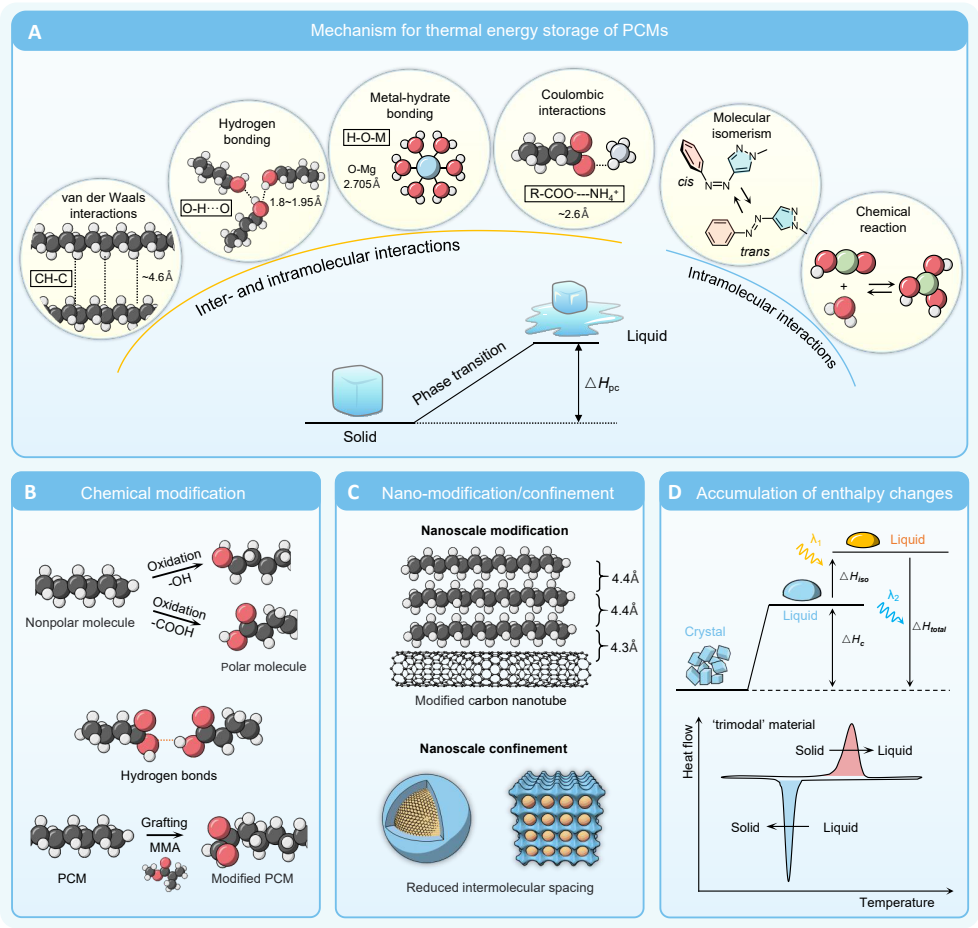

Figure 1. Mechanism and methods for increasing the enthalpy change of PCMs (A) Typical intermolecular and intramolecular interactions for PCMs and other chemical transitions. (B) Chemical modification methods for increasing the enthalpy change of PCMs. (C) Nanoscale modification and confinement methods for increasing the enthalpy change of PCMs. (D) Accumulation strategies of multiple enthalpy changes.

METHODS FOR INCREASING THE ENTHALPY CHANGE OF PCMS

Three methods for increasing the phase-change thermal storage density can be concluded from previous studies, *i.e.*, chemical modification, nano-modification/confinement, and accumulation of multiple enthalpy changes (Figure 1B-D).

Chemical modification methods such as oxidation and grafting can increase the enthalpy of fusion of PCM by enhancing the intermolecular force, which is primarily determined by molecular weight, polarity, and the degree of PCM branching. Generally, the intermolecular force increases with increasing molecular weight and polarity. Therefore, the introduction of hydroxyl, carboxyl, and carbonyl polar groups can transform nonpolar molecules into polar molecules to increase the intermolecular force, and meanwhile the introduced hydrogen atoms help to form hydrogen bonds between molecules. Moreover, chemical grafting may increase the intermolecular force by increasing molecular

weight of PCMs. For instance, the paraffin chemically modified with polar monomer acrylic could show a 7.4% enhancement of latent heat compared to the unmodified paraffin.[2]

Nanoscale modification and confinement is another approach to tune the apparent latent heat of the nanocomposite PCMs by regulating the molecular interactions. The resultant latent heat is mainly attributed to two factors: i) the intensity of molecular interactions among PCM molecules themselves and between PCMs and nanoparticles; ii) the loading weight/volume fraction of nanoparticles in PCMs. When the loading of nanoparticles is low, the molecular interaction effect is dominated. Thus, an increase in molecular interaction will improve the latent heat of PCMs. When the addition of nanoparticles increases, the content of the PCM is largely reduced. In this case, the effective latent heat will decrease because nanoparticles cannot contribute to the latent heat capacity. It should be noted that different types of nanoparticles and PCMs have different effects on latent heat. Proper surface modification of carbon nanotubes can increase the interaction with PCMs, which is beneficial for improving the latent heat of the PCMs with a load of less than 1 wt.%. Besides, confining the PCM in nano-cavity can also significantly increase the heat storage capacity of PCMs by shortening the intermolecular spacing among PCM molecules. In the nanoconfinement effect, the weak inter- and intramolecular interactions can be enhanced by shortening the intermolecular spacing due to high pressure and electric charge density, which are caused by phase transition within a confined space. For example, heat storage capacity of a nanocapsule-confinement system with stearic acid (SA) sealed in silica nanoshells can be increased to 374.2 J g^{-1}, about 36.9% higher than that of unconfined SA (273.3 J g^{-1}).[3]

Accumulation of multiple enthalpy changes is also an effective strategy for substantially improving the heat storage density by introducing an extra intramolecular force, including molecular isomerization transition, chemical bonding, etc. The isomerization transition of some compounds at molecular level has been used for molecular energy storage. The photo-switchable molecules for molecular solar thermal energy storage (MOST) as compound A (parent) can undergo a photon-induced isomerization to form photo-isomer B. B can then be triggered to switch back to A by light, heat, or a catalyst, accompanied with the release of stored energy as heat. A variety of photo-switches, such as phenylazopyrazole, norbornadiene–quadricyclane and azobenzene, have been investigated, with an aim to increase their isomerization enthalpy, ΔH_{iso}. Due to the independence of molecular isomerization conversion from the solid-liquid transition, their synergistic effect can be used to enhance the energy storage density. In this case, the isomerization enthalpy and phase change enthalpy can be accumulated in a given mass or volume of PCMs. Recently, the design of MOST compounds that undergo a phase transition from solid to liquid during light irradiation has emerged, which combines the latent heat capacity (ΔH) and isomerization enthalpy (ΔH_{iso}). This strategy has been employed to achieve a combined energy storage system that operates in condensed phases and accomplishes a gravimetric energy density over 350 J g^{-1},[4] which exceeds nearly all commonly-used PCMs within the same working temperature range of 50~100°C. Very recently, a 'trimodal' material has been reported that synergistically stores large amounts of thermal energy by integrating three distinct energy storage modes—latent, thermochemical and sensible.[5] The transition involves melting of the eutectic mixture of boric and succinic acids, which simultaneously undergoes dehydration into water and metaboric acid that dissolve into the liquid. Consequently, a record-high reversible thermal energy storage density of 394 J g^{-1} has been obtained. Overall, the changes in the phase state of the 'trimodal' material only involve the solid and solution states, so this conversion can also be called "phase change" in a broad sense. Different from conventional PCMs like paraffin waxes and fatty acids, the phase transition process of the eutectic mixture is more complex due to the dehydration reaction in an isometric space, which might be similar to that of the inorganic salt hydrates. To reveal the phase transition process, the thermodynamic phase diagram of the 'trimodal' material needs to be further studied.

SUMMARY AND OUTLOOK

Remarkable progress has been made in enhancing the heat storage density of PCM through chemical modification, nanoscale modification and confinement, and the accumulation of multiple enthalpy changes. However, achieving the higher energy storage density remains a long-term pursuit to develop advanced latent heat storage technologies, and the upper limit of phase-change thermal storage density remains unexplored. To achieve further enhancement in PCM latent heat of fusion, it is essential to elucidate the fundamental mechanisms of the latent heat of fusion and then to build precise theoretical models to illustrate the influence factors of latent heat. Advanced computational approaches, including molecular dynamics simulations and artificial intelligence techniques, will contribute to the accurate, fast and cost-effective design of PCMs with high latent heat. On this basis, more innovative methods or strategies to enhance the change of inter- and intramolecular interactions during phase transition should be explored, including physically and chemically modifying the existing PCMs and developing the novel PCMs by molecular engineering. Last but not least, the reversibility and stability of phase transition in consecutive heating and cooling cycles should be placed into priority when designing PCMs or composite PCMs. With the increased latent heat capacity and the improved cyclic stability, thermal conductivity of PCMs represents another key challenge, which needs to be addressed for improving power density in various practical applications, including thermal energy storage, electronic thermal management, building energy management, etc.

REFERENCES

1. Matuszek K., Kar M., Pringle J.M., et al. (2023). Phase Change Materials for Renewable Energy Storage at Intermediate Temperatures. *Chem. Rev.* **123**:491–514. DOI:10.1021/acs.chemrev.2c00407
2. Zhao X., Liu P. and Ye L. (2014). Synthesis, structure and phase transition property of acrylic acid grafted paraffin. *J. Mol. Struct.* **1064**:37–43. DOI:10.1016/j.molstruc.2014.02.003
3. Zhang S., Wang S., Zhang J., et al. (2013) Increasing phase change latent heat of stearic acid via nanocapsule interface confinement. *J. Phy. Chem. C* **117**:23412-23417. DOI:10.1021/jp408478h.
4. Wu S., Zhang Z., Li T., et al. (2023). Optically-controlled variable-temperature storage and upgrade of thermal energy by photoswitchable phase change materials. *ACS Mater. Lett.* **5**:2019–2027. DOI:10.1021/acsmaterialslett.3c00351
5. Saher S., Johnston S., Esther-Kelvin R., et al. (2024) Trimodal thermal energy storage material for renewable energy applications. *Nature* **636**:622-626. DOI:10.1038/s41586-024-08214-1

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AUTHOR CONTRIBUTIONS

All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.