

Particle Technology in the Formulation and Fabrication of Thermal Energy Storage Materials

Jiang, Zhu; Li, Xinyi; Jin, Yi; Zhang, Xiaosong; Tong, Lige; Wang, Li; Ding, Yulong

DOI:

[10.1002/cite.202200113](https://doi.org/10.1002/cite.202200113)

License:

Creative Commons: Attribution (CC BY)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Jiang, Z, Li, X, Jin, Y, Zhang, X, Tong, L, Wang, L & Ding, Y 2022, 'Particle Technology in the Formulation and Fabrication of Thermal Energy Storage Materials', *Chemie Ingenieur Technik*.
<https://doi.org/10.1002/cite.202200113>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Particle Technology in the Formulation and Fabrication of Thermal Energy Storage Materials

Zhu Jiang^{1,2}, Xinyi Li¹, Yi Jin³, Xiaosong Zhang^{1,2}, Lige Tong⁴, Li Wang⁴, and Yulong Ding^{4,5,*}

DOI: 10.1002/cite.202200113

 This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



Supporting Information
available online

Dedicated to Prof. Dr.-Ing. Joachim Werther on the occasion of his 80th birthday

This article reviews the state of the art of the formulation and fabrication of sensible, latent, and thermochemical thermal energy storage (TES) materials with special focus on the role of particle technology in enhancing the performance of these materials. Molten salt-based sensible TES materials have been intensively studied, particularly the use of doped nanoparticles for enhancing specific heat capacity and thermal conductivity. For latent TES, the inclusion of property enhancers is among the most effective approaches to address the low thermal conductivity and supercooling issues of phase change materials (PCMs), whereas the encapsulation of PCMs and structurally stabilized composite PCMs are the favorable methods to address leakage and chemical incompatibility challenges. Thermochemical TES materials are often incorporated with an inert or an active host matrix for structural stabilization.

Keywords: Particle technology, Phase change materials, Sensible storage, Thermal energy storage materials, Thermochemical storage

Received: June 26, 2022; *revised:* July 31, 2022; *accepted:* September 15, 2022

1 Introduction

Net-zero energy transition has different pathways in different countries. The use of renewable energy and electrification are among the most common pathways. The International Renewable Energy Association (IRENA) indicated that the share of renewable energy will increase from 19 % in 2019 to 79 % in 2050, and the share of electricity in total final energy consumption will increase from 21 % in 2019 to over 50 % in 2050 [1,2]. Due to the intermittency and fluctuation nature of renewable energy sources, energy storage is essential for meeting supply-demand mismatches. This has led to significant surge in the research and development of energy storage technologies over the past two decades. Among these technologies, thermal energy storage (TES) has a significant role to play in future zero-carbon energy systems due to the following reasons: 1) thermal energy is at the heart of the energy supply chain, with about 90 % of the world's energy budget currently centered around heat conversion, transmission, and storage; 2) thermal energy is the most important intermediate product or by-product (waste heat) [3]; and 3) over 50 % of the global final energy consumption is thermal energy [3].

A TES technology stores energy by heating or cooling a storage material when energy production exceeds demand

and makes it available later by discharging the energy from the storage material (see Fig. 1). The technology can be divided into three categories: sensible heat storage (SHS) which stores and releases heat by changing the temperature of the storage material; latent heat storage (LHS) which stores and releases energy through phase change of the material and hence is also called phase change material (PCM)-based TES; and thermochemical energy storage

¹Dr. Zhu Jiang, Xinyi Li, Prof. Xiaosong Zhang
School of Energy & Environment, Southeast University, Nanjing, 210096, China.

²Dr. Zhu Jiang, Prof. Xiaosong Zhang
Engineering Research Center of BEEE, Ministry of Education of China, Nanjing, 210096, China.

³Dr. Yi Jin³
Nanjing Jinhe Energy Materials Co., Ltd., Zhenjiang, 212499, China.

⁴Prof. Lige Tong, Prof. Li Wang, Prof. Yulong Ding
School of Energy & Environmental Engineering, University of Science & Technology Beijing, Beijing 100083, China.

⁵Prof. Yulong Ding
y.ding@bham.ac.uk
Birmingham Centre for Energy Storage & School of Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, UK.

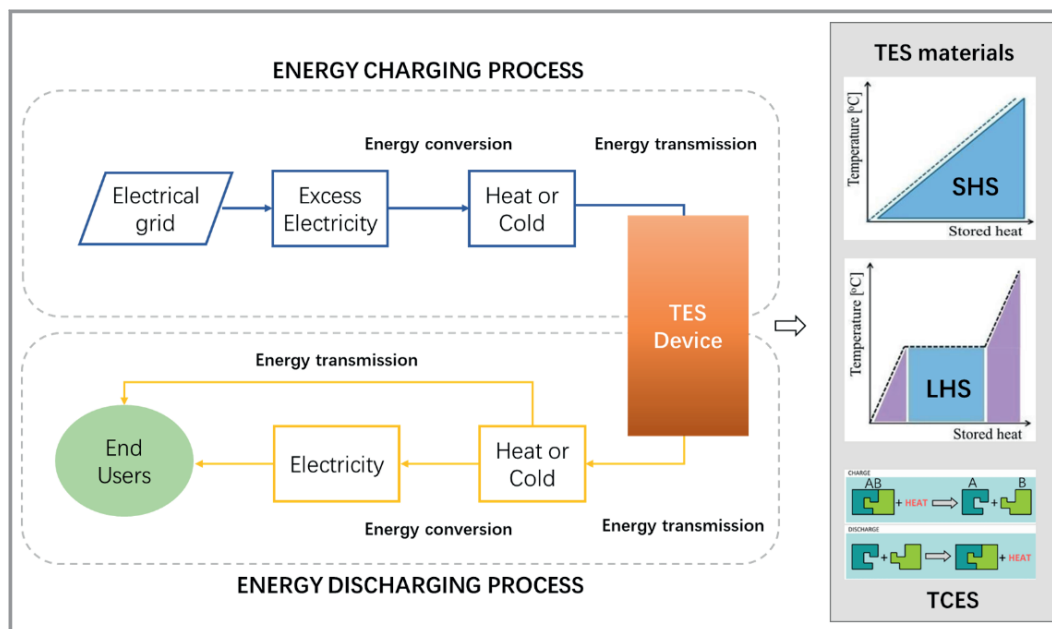


Figure 1. Thermal energy storage (TES) principle and classification according to TES materials.

(TCES) which uses reversible sorption and/or chemical reactions to store and release energy.

TES is not a new technology but still faces some scientific and technological challenges that hinder large-scale wide-range deployments, e.g., its relatively low power density and slow response speed compared with other energy storage technologies, such as batteries, and supercapacitors. Besides, the dissipation of thermal energy over time is unavoidable for sensible and latent heat-based TES technologies. As illustrated in Fig. 1, the TES material forms the major part of a TES system, thus impacting the overall performance of the system, particularly energy storage density, charging and discharging kinetics, cost-effectiveness, and life span. In recent years, a large number of studies have addressed scientific and technological challenges associated with TES materials. They are summarized in the following:

- material screening: developing a protocol to screen reliable TES materials with high energy density, good thermal conductivity, long lifespan, good safety, and low costs
- formulation: addressing issues associated with pure TES materials, such as low thermal conductivity, supercooling, and low cyclability, through the formulation of composite TES materials
- manufacturing: examining cost-effective and scalable manufacturing routes for TES materials [4]

This article pays specific attention to the role of particle technology in the TES materials formulation and manufacturing, as many as-received raw materials and property enhancers for TES are in granular form over a wide size range from nano- to over millimeter scale. The processing of these particles (e.g., milling, mixing, compaction, sintering, dispersion) and their characteristics (e.g., particle size, shape, surface area, pore structure, surface roughness, sur-

face energy, hardness, Young’s modulus) can significantly affect the properties of the TES material at both particle and module levels as well as the charging/discharging kinetics due to their effects of heat and mass transfer and reaction kinetics (for thermochemical storage). Besides, the interactions between particles or between particles and liquids can significantly affect the structure developments as well as the thermal and physical properties of the TES materials [5, 6]. Therefore, particle technology is highly relevant to thermal energy storage material research and development. As the three types of TES (sensible, latent heat, and thermochemical) technologies use different storage materials, diverse scientific challenges exist, and this review is structured according to the three categories.

2 Particle Technology in Sensible TES Materials – Molten Salt-Based Nanosuspensions

2.1 Property Enhancement of Molten Salts

Sensible TES materials refer to a group of materials that store thermal energy by varying their temperatures, with the stored heat proportional to density, specific heat, volume, and temperature variation of the storage materials. Molten salts are among favorable sensible TES materials and have been deployed in concentrating solar power (CSP) system both as the energy carrier and the storage medium due to their wide working temperature range, high thermal stability, and low vapor pressure. However, key challenges of molten salts for CSP lie in relatively low energy density and low thermal conductivity (and thus limited power

density). The addition of nanoparticles to the molten salts to form nanosuspensions (often termed nanofluids in the literature) has been one of the most studied methods to address the challenges.

2.1.1 Heat Capacity Enhancement

A higher specific heat capacity leads to a smaller size of the storage system, a lower cost to transfer and store thermal energy, and thus cheaper electricity production [7]. Shin et al. [8] were among the first who reported that the addition of a small amount of silica nanoparticles (no more than 1 wt%) into carbonate eutectic could increase the specific heat capacity up to 24%. This enhancement in specific heat capacity has also been reported by dispersing different nanoparticles: CuO [9], Al₂O₃ [10–12], TiO₂ [13], and graphene nanoplatelets (GNPs) [14]. Different concentrations have different effects on the thermophysical properties of molten salt. An appropriate concentration of nanoparticles could enhance the thermal properties of the molten salt, on the contrary, inappropriate concentration of the nanoparticles, e.g., an extremely high concentration, could give unfavorable thermal properties due to high extent of nanoparticle agglomeration [15].

Shin and Banerjee [16, 17] made an attempt to interpret the mechanisms of the enhancement in specific heat capacity due to the addition of nanoparticles and proposed three possible mechanisms. The first mechanism is that the high surface energy of nanoparticles leads to an enhanced heat capacity of particles at nano levels. The second mechanism is due to interactions between the surface atoms of nanoparticles and molten salt. Such an interfacial interaction between the nanoparticles and molten salt could lead to an additional thermal storage of the nanofluid. The third mechanism is due to the formation of a semi-solid layer with enhanced thermophysical properties around the nanoparticles. However, the minimal addition of nanoparticles limits the possibilities of any of these mechanisms. Recently, another theory attributes the enhancement in heat capacity to the formation of dendritic nanostructures (see Fig. 2) which was also experimentally observed by scanning elec-

tron microscopy (SEM) [18]. The high specific surface energy of nanoparticles makes it easy to form nanostructures, leading to increased specific heat of the molten salt nanocomposite. Shin and Tiznobaik [19] investigated this effect experimentally by controlling the formation of nanostructures and concluded that the nanostructure was responsible for the enhanced specific heat capacity of molten salt nanofluids. Tiznobaik et al. [20] regarded the enhancement of the specific heat capacity less sensitive to the material composition of the nanoparticles but dominated by the formed nanostructures.

2.1.2 Thermal Conductivity Enhancement

Numerous studies on the enhancement of thermal conductivity of water- and oil-based nanofluids can be found in the literature. With increased interest in molten salts, the impact of the addition of nanoparticles on the thermal conductivity of molten salts has also been investigated. Myers Jr. et al. [21] doped nitrate salts with CuO nanoparticles and showed significant enhancements up to ~72% over different temperature ranges for different nitrate salts. Awad et al. [22] investigated the thermal property enhancements by dispersing Fe₂O₃, TiO₂, and CuO into KNO₃ and solar salt (NaNO₃-KNO₃). Solar salt doped with Fe₂O₃ was shown to give the most effective thermal diffusivity enhancement by up to 60%. Yu et al. [15] dispersed a mixture of SiO₂ and TiO₂ nanoparticles into molten salt and found a better enhancement of thermal conductivity compared with dispersing the single nanoparticles into the salt separately. They inspected the microstructures of the nanosuspensions, and observed dense nanostructures and heat transfer channels, which could be the reasons for the enhanced specific heat and thermal conductivity.

2.1.3 Increased Viscosity

Viscosity is an important parameter for heat transfer fluids in CSP plants as it determines pumping power and also the convective heat transfer coefficient [23–25]. Lasfargues et al. [24] investigated the rheological behavior of solar salt doped

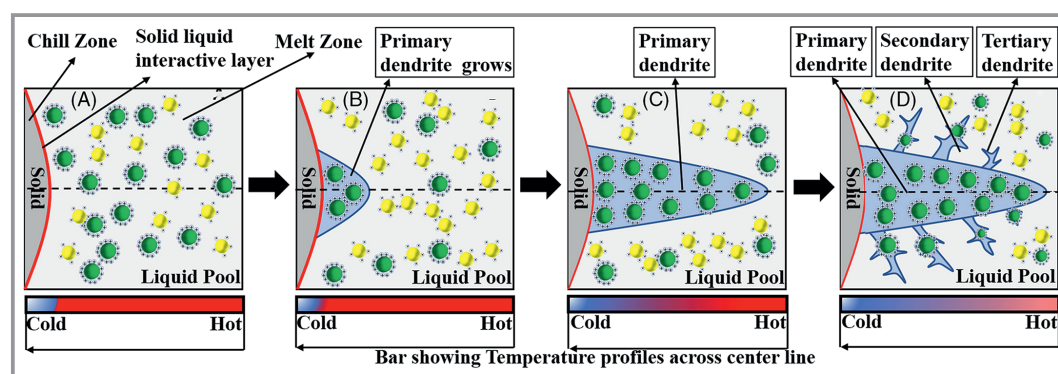


Figure 2. Nucleation and the grain growth of a dendritic structure in a molten salt nanofluid (reproduced from [18] with permission from Wiley).

with 0.1 wt % CuO and observed a viscosity increase of 5.0 to 18.0 % at different temperatures. Byeongnam et al. [26] studied the alkali carbonate eutectic salts dispersed with multi-wall carbon nanotubes (MWCNTs) and found a significant increase in viscosity of up to 93 % with 2 wt % MWCNT. The viscosity increase depends on several factors including particle size and shape, particle concentration and extent of particle aggregation, and the presence of surfactants/dispersants [27]. Far et al. [28] observed the formation of a dendritic nanostructure when salt crystallizes on a nanoparticle surface. The formation of the nanostructures and the aggregation of nanoparticles are regarded as the primary reasons for the viscosity increase. They also found that the addition of NaOH to the nanofluids could disrupt the formation of dendritic nanostructures, thus reducing the heat capacity enhancement and the viscosity increase [29]. The use of surfactants/dispersants, low nanoparticle concentrations, or an appropriate particle size could effectively decrease the viscosity of nanosuspensions [30].

2.2 Fabrication of Molten Salt-Based Nanosuspensions

The methods for the fabrication of nanosuspensions can be classified into two categories: two-step method and one-step

method (see Tab.1). The two-step method includes a first step to prepare the nanoparticles and a second step to disperse the nanoparticles into a base fluid, while the one-step method combines the preparation of the nanoparticles and the dispersion of nanoparticles in a single step. Compared with the two-step method, the one-step method has advantages such as smaller particle size, less agglomeration, and high dispersion stability. However, the one-step process is expensive and difficult to scale up. In addition, the volume concentration of nanoparticles prepared by the one-step method is often limited [63].

2.2.1 Two-Step Method

The fabrication of molten salt-based nanofluids often requires a high-temperature environment. Given the oxidative and corrosive nature of high-temperature salts, a modified two-step method has been widely used for the fabrication. Fig. 3 schematically shows the process. Nanoparticles and salts are dissolved in a solvent (usually water) under sonication at low temperature to break down the agglomeration and obtain a homogeneous suspension. Subsequently, an evaporation process is used to remove the solvent (water) from the homogeneous suspension. In this process, boiling should be avoided to prevent the agglomeration of nanoparticles [65].

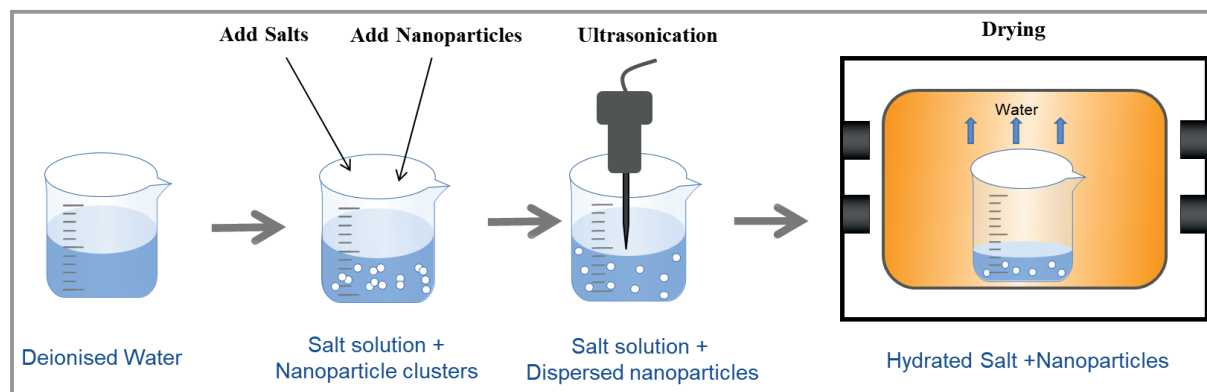


Figure 3. Modified two-step method for high-temperature molten salt-based nanofluids.

Table 1. Comparison between two-step and one-step methods (reproduced from [64] with permission from the Royal Society of Chemistry).

Methods	Two-step method	One-step method
Advantages	simple in process and devices	high uniformity of the nanoparticle sizes
	economic and scaleable to large scale	smaller nanoparticle size
	applicable to the dispersion of various nanoparticles	less agglomeration
Disadvantages	more agglomeration	high stability of the nanofluids
	lower stability of the nanofluids	high cost in fabrication
		small yield
		introduction of impurities

Sonication is considered to be an effective way to deagglomerate nanoparticles in molten salts [30]. Lasfargues [40] used a ball mill to directly grind and mix a eutectic salt ($\text{NaNO}_3\text{-KNO}_3$) with CuO and Ti_2O nanoparticles in solid state and found that nanoparticles are aggregated, which could not be dispersed and an interconnected layer was formed. Zhang et al. [52] investigated the effects of ultrasonication time on nanoparticle dispersion and the associated enhancement in heat capacity. They found that ultrasonication time had a great impact on the nanoparticle dispersion, a longer or shorter time both led to a lower enhancement in heat capacity. A dispersion time of 50 min was found to be optimal in a range from 0 to 200 min, due to the formation of lamellar structure in the molten salt.

Molten salt-based nanofluids are mostly manufactured at laboratory level, owing to the energy- and time-consuming process and the potential agglomeration involved in the drying process. Schuller et al. [66] introduced a spray drying method practiced in food and drug sectors to obtain flash evaporation of the water solvent. They observed that the nanofluids prepared by air drying presented higher specific heat, lower latent heat, and similar melting temperature as the one evaporated in a hot plate. To scale up the manufacturing process, a customized dispersion device has been explored for direct high-temperature dispersion. For example, Ho et al. [67] built a high-temperature dispersion device coupled with mechanical stirring. They found that with mechanical stirring at 350°C for 180 min, a homogeneous $\text{Al}_2\text{O}_3/\text{KNO}_3\text{-NaNO}_2\text{-NaNO}_3$ nanosuspension could be obtained. However, this device showed limitation when the concentration of Al_2O_3 nanoparticles was higher than 0.016 wt %, when serious agglomeration was obtained.

2.2.2 One-Step Method

This method can be done via a physical route or a chemical route. However, the physical method, particularly the vapor deposition method, can only be used on low vapor pressure base fluids [65]. Thus, the chemical method is more widely used to synthesize high-temperature nanofluids due to greater thermal stability of molten salts.

Lasfargues et al. [13] were among the first who used an in situ method to produce TiO_2 -doped nitrate salt-based nanofluids via the one-step route (see Fig. 4). In their method, 1 to 3 wt % of TiOSO_4 was used as a precursor and dispersed in a nitrate salt. The mixture was heated

to 450°C to obtain TiO_2 nanoparticles following the decomposition process of $\text{TiOSO}_4 \rightarrow \text{TiO}_2 + \text{SO}_2 + 1/2 \text{O}_2$ [68]. The obtained nanofluids showed a homogeneous dispersion with an average size of the TiO_2 nanoparticles of 16.35 nm. Subsequently, Lasfargues et al. [39] applied the same method to produce $\text{CuO}/\text{KNO}_3\text{-NaNO}_3$ nanofluid by using $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ as precursor. The CuO nanoparticles were obtained by decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ at 450°C via $\text{CuSO}_4\cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3$. Although different percentages of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.25 to 5 wt %) were investigated, the particle size of the CuO nanoparticles obtained was found heterogeneous. Luo et al. [41] used a similar chemical method to produce $\text{CuO}/\text{solar salt nanofluids}$. In their work, $\text{CuC}_2\text{O}_4\cdot 0.5\text{H}_2\text{O}$ was used as the precursor via $\text{CuC}_2\text{O}_4\cdot 0.5\text{H}_2\text{O} \rightarrow \text{CuO} + \text{CO} + \text{CO}_2 + 0.5\text{H}_2\text{O}$. TEM results suggested that the synthesized CuO particle be in the range of 10–20 nm, with a slight extent of agglomeration. Huang et al. [44] prepared a $\text{MgO}/\text{solar salt nanofluid}$ by decomposition of $\text{Mg}(\text{OH})_2$. The produced spherical MgO nanoparticles showed a particle size between 50 and 200 nm. Although the one-step method is regarded as a more effective way to fabricate well-dispersed nanofluids than the two-step method, reported studies indicated that isolated nanoparticles are hard to obtain and a certain degree of agglomeration is difficult to avoid. In addition, more work is needed on the percentage of the precursor and the fabrication conditions so that the chemically synthesized nanoparticles have a narrowly distributed particle size and the residue of unreacted precursors is minimized.

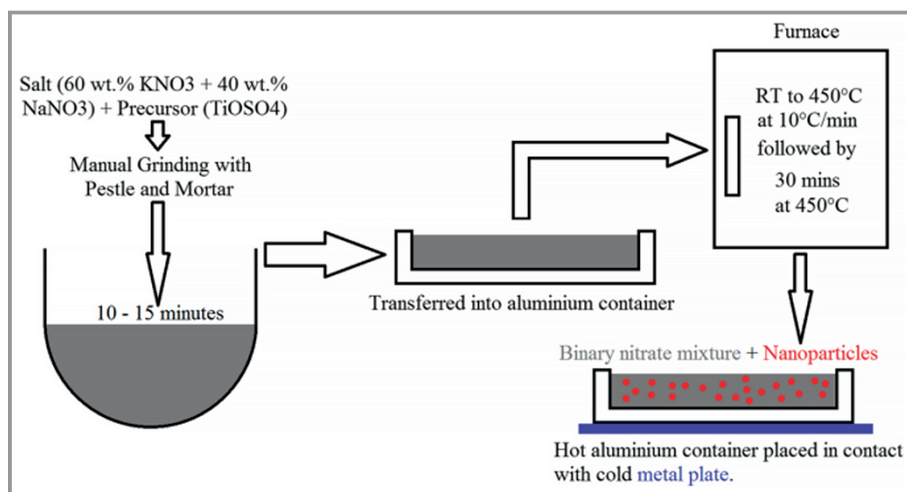


Figure 4. Schematic diagram of the in situ preparation method of TiO_2 dispersed nitrate salt nanofluid (reproduced from [13], no permission required).

3 Particle Technology in Latent Heat Storage Materials

3.1 Property Enhancement

Latent heat storage materials, more often termed as phase change materials (PCMs), store heat through phase transition, e.g., liquid-solid, of the materials. PCMs are favored for the benefits of high energy density and nearly isothermal process during energy charging and discharging. However, there remain key challenges, particularly, low thermal conductivity of nonmetallic PCMs, supercooling of many salt hydrate- and sugar alcohol-based PCMs, chemical incompatibility of many corrosive PCMs, shape destabilization and the associated leakage. Some of these challenges could be addressed by using particles and/or matrices, which will be illustrated in the following subsections. Furthermore, a general approach to address the chemical incompatibility and shape destabilization during phase change is the formation of a core-shell structure (PCM capsules) or a shape-stabilized composite (shape-stabilized composite

PCM (SSCPCM)) by the so-called encapsulation method. Therefore, the formulation and fabrication of PCM capsules and SSCPCMs is also covered here.

3.1.1 Enhancement of PCM Thermal Conductivity

Most nonmetallic PCMs show a low thermal conductivity below $\sim 0.5 \text{ W m}^{-1}\text{K}^{-1}$, which significantly limits the charging/discharging kinetics in practical applications. Dispersion of highly thermally conductive particles and/or insertion of a thermally conductive matrix have been the most widely used methods to improve the thermal conductivity of PCMs. The thermally conductive enhancers include zero-dimensional, one-dimensional, two-dimensional, and three-dimensional structured additives. Different structured additives can lead to the formation of different heat conduction networks. Besides, mass fraction, intrinsic thermal conductivity, and particle size of the additives are also key parameters that determine the effects of the enhancers [69]. Tab.2 summarizes the additives for PCM thermal conductivity enhancement.

Table 2. Additives for thermal enhancement of PCMs. SWNT, single-wall carbon nanotubes; S-SWNT and L-SWNT, short and long single-wall carbon nanotubes; MWCNT, multi-wall carbon nanotubes; NPs, nanoparticles; CF, carbon fibre; BN, boron nitride; EG, expanded graphite.

Thermally conductive enhancers (TCEs)		PCM		Enhancement of thermal conductivity		Ref.
Material	$k_{\text{TCE}} [\text{W m}^{-1}\text{K}^{-1}]$	Material	$k_{\text{PCM}} [\text{W m}^{-1}\text{K}^{-1}]$	Mass fraction of TCEs	Enhancement	
<i>Zero-dimensional additives</i>						
graphite powder	130	SA	0.26	0.1 vol %	8.79 %	[70]
Au NPs	318	PEG	0.398	3.3 wt %	10.2 %	[71]
Cu NPs	400	SAT	0.59	0.5 %	20 %	[72]
<i>One-dimensional additives</i>						
CF	900	erythritol	0.733	25 vol %	41 times	[73]
MWCNTs	$\sim 2000\text{--}3000$	$\text{C}_{12}\text{H}_{24}\text{O}_2$	0.215	1 vol %	171 %	[74]
S-SWNTs, L-SWNTs	~ 4000	carbonate eutectic salts	0.516–0.667	1 wt %	42.25 %	[58]
SW carbon nano-horns	~ 27 (from EMT model)	$\text{C}_{12}\text{H}_{24}\text{O}_2$	0.215	1 vol %	27 %	[74]
<i>Two-dimensional additives</i>						
graphite flake	1.1	$\text{C}_{12}\text{H}_{24}\text{O}_2$	0.215	1 vol %	223 %	[74]
BN	0.53	paraffin	0.38	10 wt %	139 %	[75]
graphene	3000	SA	0.26	0.1 vol %	15.2 %	[70]
EG	129	PEG	0.35	10 wt %	103 %	[76]
<i>Three-dimensional additives</i>						
carbon foam	0.43	paraffin	0.25	7.8 wt %	172 %	[77]
aluminum foam		PEG	0.35	30 wt %	156.6 %	[78]
copper foam	398	paraffin	0.487		40 %	[79, 80]
nickel foam	91.4	paraffin	0.2	80 %	500 %	

Constructing an effective conductive pathway/network with thermal conductivity enhancers is the ultimate goal to achieve high thermal conductivity enhancement in PCMs. 0D materials with an inherently high specific surface area are required to have a good dispersion, thus constructing an interconnected conductive network, 1D additives take the advantage of their own structure and high thermal conductivity to establish linear thermal conduction, 2D additives could establish efficient in-plane thermal conduction with their lamellar structure, whereas 3D additives could offer an intrinsic 3D conductive network [76].

Zero-Dimensional Additives: The zero-dimensional additives here refer to isotropic micro- and nanoparticles, such as spherical graphite, Cu, Al, and TiO₂ nanoparticles. These particles have a large specific surface area and a strong interparticle interaction. Li et al. [81] doped paraffin with 1–2 wt % of Al powder and showed that the energy discharging rate was increased by 36 %. CuO was employed by Cui et al. [71] to improve the thermal behavior of sodium acetate trihydrate (SAT). They observed a thermal conductivity increase of 20.5 % with an addition of 0.5 wt % CuO. Tang et al. [72] added Al₂O₃ into a form-stable PEG/SiO₂ composite PCM via an ultrasound-assisted sol-gel method. With the addition of 3.3 wt % Al₂O₃, the thermal conductivity was found to increase by 12.8 %. Methods for achieving a better dispersion of the particulate additives in PCMs include the addition of surfactants and surface modifiers and the application of pH control (for aqueous systems) and ultrasonic vibration during manufacturing [72].

One-Dimensional Additives: Fibrous and rod-like thermally conductive enhancers usually present a great length-to-diameter ratio and an anisotropic heat transfer behavior. Carbon fiber (CF) and carbon nanotubes (CNTs) are typical one-dimensional additives. CNTs including single/multi-walled CNTs (SWCNTs/MWCNTs) possess a high thermal conductivity in the axial direction, reaching values as high as 2000–6000 W m⁻¹K⁻¹ [76, 82]. Such 1D materials have been shown to enhance the thermal conductivity of a lauric acid by 171 and 27 % with 1 vol % MWCNTs and SWCNTs, respectively [74]. The high aspect ratio and high thermal boundary conductance are found beneficial for thermal conductivity enhancement. Besides, the thermal interface conductance between the nanomaterial and organic interface was an order of magnitude higher in the solid state compared to that in the liquid state [74]. Tao et al. [58] interpreted that the enhancement of thermal conductivity was directly related to nanomaterial microstructure; nanomaterial with a columnar structure could form a more effective heat conduction network.

Two-Dimensional Additives: Additives with lamellar structure, such as graphene nanosheets, graphite flakes, hexagonal boron nitride (h-BN) flakes, and layered expanded graphite (EG), conduct heat in two directions. Wang et al. [83] observed that with an addition of 24 wt % EG the thermal conductivity of a PCM composite increased by up to 24 times due to the exceptional thermophysical

properties of EG. Besides, the PCM was found to be retained in the inner structure of EG, indicating no need for extra encapsulation. They also proposed a model to predict the effective thermal conductivity of the composites [76]. BN is an interesting material, which is electrically insulating but highly thermally conductive. Single-layered BN was found to have a higher thermal conductivity than multi-layered BN due to interlayer phonon scattering [84]. Hu et al. [85] prepared BN aerogel by a controlled anisotropic freeze casting method, which was subsequently infiltrated with the epoxy resins to obtain a PCM composite. The oriented BN matrix was shown to have a better thermal conductivity compared with the conduction network formed by randomly distributed BN flakes.

Three-Dimensional Additives: Advantages of 3D additives, such as carbon foam, copper foam, and nickel foam, are the continuous 3D network and high contact area with the PCM for heat transfer. These foam-structured matrices possess a high porosity for retaining the PCM and, thus, have been widely studied as matrix to compound with less thermally conductive PCMs. Carbon foam is a class of low-cost 3D carbon materials that can be produced from a wide range of biomass materials. Wang et al. [82] fabricated a mesoporous carbon matrix via the carbonization of sucrose at different temperatures. A higher degree of graphitization demonstrated a higher thermal conductivity of the carbonic matrix, leading to a higher overall thermal conductivity when impregnated with PCM. Sheng et al. [77] used biomass cotton to produce carbon sponges with different thicknesses to retain paraffin. It was found that a greater thickness of the carbon sponge led to a higher overall thermal conductivity of the PCM composite, owing to the robust thermally conductive pathways. Metal foams are versatile matrices with high surface area, thermal conductivity, and porosity and have a good mechanical strength. Wang et al. [80] found that the insertion of foam copper in PCM can reduce the energy charging time by more than 40 %. Hussain et al. [79] investigated the performance of a nickel foam-paraffin composite for battery thermal management and showed that the battery surface temperature decreased by 31 and 24 % compared with pure paraffin. It should be noted that the porosity of metal foams is often designed according to the application requirements. Low porosity foams are often designed for enhancing heat transfer, while high porosity foams are designed for a high heat storage capacity.

3.1.2 Suppressing PCM Supercooling

Supercooling is a phenomenon that describes a PCM in its liquid state at a temperature lower than its solidification point. The degree of supercooling depends not only on the nature of the materials, but also the cooling rate, the amount of sample, the surface for nucleation, and PCM thermal history. The phenomenon can be either useful or harmful depending on the actual application. It is always

regarded as a drawback for thermal energy storage applications due to undesirable unstable and probabilistic performance – the higher the degree of supercooling, the lower the amount of latent heat that can be used [86].

The introduction of a nucleating agent is the most used method to reduce supercooling as metastable supercooled systems are exceedingly susceptible to additional particles, impurities, and surfaces. The nucleating agents can be divided into isomorphous, isostructural, and epitaxial nucleators based on the crystal structure. Isomorphous and isostructural nucleators both possess the same crystal structure and atomic connectivity as the PCM crystals. In addition, isomorphous nucleators also have virtually identical unit cell dimension and chemical composition as the PCM crystals [87], which contributes to rapid crystallization around the nucleators. Epitaxial nucleators have a different crystal morphology compared to the PCM, the nucleator mainly offers a favored position for the PCM molecules to attach, deposit, and crystallize [87].

Salt hydrates and sugar alcohols tend to have a relatively severe supercooling degree up to several to tens of degrees [88]. To ease the supercooling of these PCMs, borax, SiO₂, and graphite powder, etc. have been widely investigated. Feng et al. [89] added borax into Na₂SO₄·10H₂O with a mass fraction of 1 to 5 wt % and showed that the supercooling degree reduced from 9 to 2 °C with 5 wt % of borax. Li et al. [90] found that the addition of SrCl₂·6H₂O as nuclei can suppress the supercooling of CaCl₂·6H₂O, and the supercooling degree did not reduce monotonously with the addition of SrCl₂·6H₂O. An optimal addition of SrCl₂·6H₂O was found to be 3 wt % at which the supercooling degree was reduced to 2.8 °C. A further increase in the SrCl₂·6H₂O addition increased the supercooling degree to 4.1 °C. These researchers also found that the use of 1.2 wt % expandable graphite oxide (EGO) in CaCl₂·6H₂O could further reduce the supercooling to ~0.6 °C.

The use of nanoparticles to suppress the supercooling of PCMs has gained attention due to the high specific surface area of nanoparticles. Yang et al. [91] added a small amount (0.05–0.3 wt %) of nanoparticles (C, Cu, and ZnO) to an erythritol-based PCM and investigated the crystallization process of the composites. They found that the supercooling degree of erythritol decreased with increasing nanoparticle addition, and carbon showed a better effect than the Cu and ZnO nanoparticles. Wu et al. [92] investigated the effect of various SiO₂ nanoparticles on the supercooling of salt hydrates and found that aerosol SiO₂ presents the most effective performance. They also observed strong polar hydroxyl bonds on the surface of aerosol SiO₂ and the ion-exchange attractions between the hydroxyl bonds and the hydrate salts and interpreted this as the main reason for the suppression of supercooling. Li et al. [93] added 0.5 wt % of γ -Al₂O₃, TiO₂, Cu, and SiO₂ nanoparticles into CaCl₂·6H₂O as nucleators and observed the reduction of the supercooling degree of CaCl₂·6H₂O to 0.2, 2.2, 5.4, and 9.5 °C, respectively. They also discussed the impact of the specific surface

free energy between the crystal nuclei and CaCl₂ solution (σ_{SB}) and suggested a smaller value of σ_{SB} and the associated smaller contact angle (θ) would benefit the crystal growth and the suppression of the supercooling.

The concentration and the characteristics of the nucleating agents have a great impact on the crystallization of PCMs as illustrated in Tab. 3 [91]. Many studies suggested that the supercooling degree decreases with increasing amount of nucleation agents, but some studies found that the increase of the concentration would not be the key reason for the suppression of supercooling [89, 92]. It should be noted that the addition of the additives also compromises the latent heat due to their non-phase-change behavior. Therefore, there is a need for studying the optimal concentration of the nucleation agents. Apart from the use of nucleation agents, mechanical and electrical triggers have also been studied to address the supercooled PCMs, which will not be discussed further here as they are beyond the focus of this article.

Table 3. Nucleation agents and suppress of supercooling degree (edited from [91]). PCM: erythritol.

Nucleation agents	Mass ratio [%]	Without nucleation agent	With nucleation agent
		Supercooling degree [°C]	Supercooling degree [°C]
C	0.05	34.5	18.6
	0.1	34.5	17.7
	0.2	34.5	17.2
Cu	0.3	34.5	16.2
	0.05	34.5	25.6
	0.1	34.5	24.3
ZnO	0.2	34.5	22.2
	0.3	34.5	18.6
	0.05	34.5	24.6
	0.1	34.5	22.1
	0.2	34.5	18.2
	0.3	34.5	16.4

3.2 Formulation and Fabrication of PCM Capsules

Encapsulation of PCMs is among effective measures to avoid direct contact of PCM with the containing environment, hold the shape from deformation, and prevent leakage. It can also enhance the heat transfer by allowing the direct contact between the encapsulated PCMs and heat transfer fluids (HTFs). There are two general ways to encapsulate PCMs, encapsulation in a core-shell structure (PCM capsules) and in a matrix to form shape-stabilized

composite PCMs [4]. The PCM capsules could be designed with mono- or polynuclear structure with a single- or multi-layered shell (see Fig. 5).

The shell material can be classified into three categories: metallic (i.e., stainless steel, Ag nanoparticles, etc.), inorganic (i.e., SiO_2 , TiO_2 , CaCO_3 , etc.), and organic particularly polymeric (polystyrene, urea formaldehyde, etc.) materials [94–102]. Metallic and inorganic encapsulation provides a high mechanical strength and good thermal stability. Both methods can be used for high-temperature applications. However, metallic shells show a high corrosion potential and are expensive. On the contrary, polymeric shells are cost-effective, but the thermal enhancement performance is indistinctive with weak mechanical strength and low thermal stability (below $400\text{ }^\circ\text{C}$) as well as flammability [103].

PCM capsules can be divided into three types according to the size of the capsules: macro-encapsulation ($>1\text{ mm}$), micro-encapsulation ($1\text{ }\mu\text{m}$ – 1 mm), and nano-encapsulation ($<1\text{ }\mu\text{m}$). In the case of micro- and nano-encapsulation, particle size distribution and particle morphology greatly affect the final performance of the PCM. PCM capsules are also helpful with heat transfer due to small sizes and large surface areas. Yamagishi et al. [104] studied the relationship between capsule structure stability and particle size and found that the breakage rate decreased significantly with decreasing particle size. Only 10% of PCM capsules with a size of 20 – $100\text{ }\mu\text{m}$ had broken after 7000 times circulation, whereas capsules with a size of 1000 – $1500\text{ }\mu\text{m}$ had broken quickly during pumping.

Most attention in this area has been paid to the use of organic shell materials [105]. Such a type of material is the most extensively studied, leading to more than 50 different known polymers as shell materials for microcapsules [106]. However, polymeric shells show low thermal conductivity, slow thermal response, and chemical incompatibilities, and they do not work at high temperatures [107]. An alternative is the use of inorganic materials for microencapsulation, which offer higher mechanical strength and thermal conductivity. Examples include SiO_2 , CaCO_3 [108], and TiO_2 [109] microcapsules produced via interfacial or in situ polymerization. SiO_2 is the most studied one and paraffin/ SiO_2 micro- and nano-capsules have been prepared by spray drying, interfacial polymerization, interfacial polycondensation, and emulsion polymerization among other methods [110]. Other inorganic materials, such as AlOOH [111], have also been used, although to a lower extent. It should be noted that the use of inorganic shells is highly

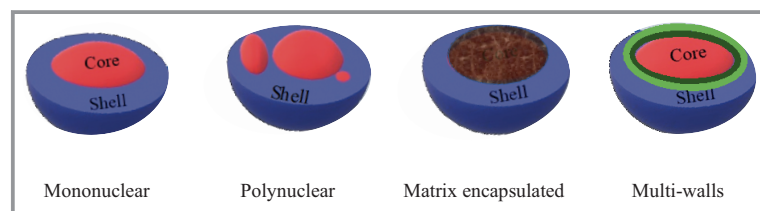


Figure 5. Core-shell structured PCM capsules.

dependent on the core/shell encapsulation method. For high-temperature PCMs, such as molten salt and metals, very few studies have been carried out. These few studies include molten salt encapsulation with perhydropolysilazane (PHPS), a ceramic precursor resin [112], SiO_2 [113], alloys like zinc (shell organo-phosphorus based), and Al-Si (Al_2O_3 shell) [111].

Micro-/nanoencapsulation of PCMs can be achieved by different fabrication routes [114]. Tab. 4 summarizes the characteristics and fabrication methods of different types of PCMs. Micro-/nanoencapsulation methods aim to produce defined and uniform particle sizes, mechanically and chemically stable capsules, and a high core-to-shell ratio of the PCM capsules. The fabrication methods can be divided into chemical, physical, and physicochemical methods:

- Chemical methods involve in situ polymerization, where the polymerization reaction and the microencapsulation occur in the same solution [115]. The in situ polymerization methods include emulsion, suspension, and interfacial methods.
- Physical methods include spray drying, solvent evaporation, centrifugal extrusion, and fluidized-bed processes. Compared to the chemical method, the physical method cannot produce microcapsules smaller than $100\text{ }\mu\text{m}$. Therefore, chemical methods are more favorable in preparing micro-/nano-encapsulated PCMs [116].
- Physicochemical methods represent the formation of the shell by both chemical and physical processes, which includes sol-gel and coacervation method.

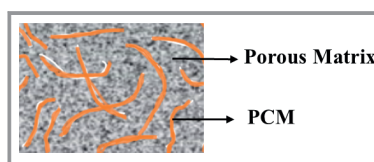


Figure 6. Structurally stabilized composite PCMs.

3.3 Formulation and Fabrication of Shape-Stabilized Composite PCMs

Structurally stabilized composite PCMs (SSCPCMs), also termed as form-stable composite PCMs (FSCPCMs), behave like solid-solid PCMs during phase transition. In the SSCPCMs, the porous structure of the matrix and/or the interparticle spaces can retain the melted PCM by capillary force, therefore showing a stable structure without leakage (see Fig. 6). SSCPCMs offer the benefits of shape stabilization, substantially reduced or eliminated corrosion, reduced phase segregation, enhanced thermal conductivity, and sometimes suppressed supercooling [117].

The SSCPCMs can be broadly classified according to the matrix materials, e.g., ceramic, carbon, metal, and polymer. Advantages of

Table 4. Characteristics and fabrication methods of different types of PCM capsules (reproduced from [64] with permission from the Royal Society of Chemistry).

Shell materials	Preparation methods	Advantages	Disadvantages	Applications
<i>Polymeric</i>				
polymethyl methacrylate (PMMA)	chemical methods: suspension; dispersion, emulsion, in situ and interfacial polymerization; polycondensation	various shell materials cost-effective	relatively low thermal stability	medium- and low-temperature applications, e.g., building cooling, refrigeration, electronic cooling, food storage and transport; thermoregulating fabric
maleimine formaldehyde (MF) resin			low mechanical strength	
copolymer poly(urethane-urea)	physicochemical methods: coacervation, layer-by-layer assembly, sol-gel encapsulation		low thermal conductivity	
styrene (St)	physical methods: spray-drying, electrostatic encapsulation			
methyl methacrylate (MMA)				
polystyrene				
<i>Inorganic</i>				
SiO ₂ , TiO ₂ , Na ₄ SiO ₄ , CaCO ₃	sol-gel method, electroless coatings	high thermal and chemical stability high mechanical strength	porous shell structure	high-temperature applications, e.g., power generation
<i>Metallic</i>				
stainless steel, carbon steel, nickel-chromium, nickel	electroplating, pre-formed, electroless	high thermal stability high mechanical and wear strength high thermal conductivity	low corrosion resistance high cost in materials and fabrications large in capsule size	high-temperature applications, e.g., concentrated solar power systems (using liquid metal as heat transfer fluid); waste heat recovery

ceramics as structural materials are good chemical compatibility, thermal stability, and absorbability [6, 118, 119], with diatomite, vermiculite, sepiolite, expanded perlite, SiO₂, and MgO being examples. Ceramic materials are often used to retain high-temperature salt-based PCMs, e.g., nitrates, carbonates, sulfates [120, 121]. Carbon-based materials are highly thermally conductive, which makes them ideal to be a matrix for PCMs with low thermal conductivity, e.g., paraffins [122]. Metallic matrices, also referred to metal foams, have a high open porosity, a great mechanical strength, and a continuous skeleton structure for efficient heat conduction. Polymeric matrices are cost-effective, chemically stable, and long-term durable, whereas they also suffer from low thermal conductivity issues and high flammability. Tab. 5 provides a summary of these matrices.

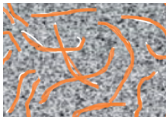
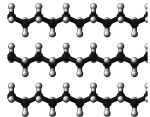
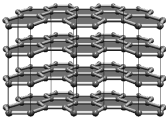

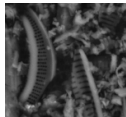
3.3.1 Impregnation Method

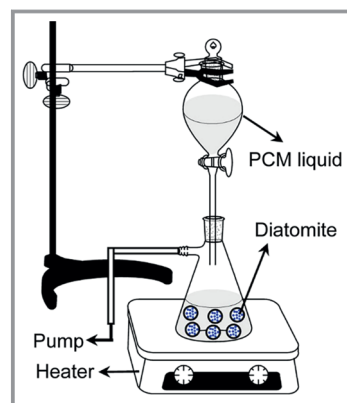
The preparation methods for different SSCPCMs have been reviewed [4]. Impregnation and mix-sintering are among the most studied fabrication methods that fall right into the scope of particle technology. The impregnation method is a process of submerging a matrix in a liquid PCM for impregnation. The impregnation methods can be further classified

into melt impregnation, vacuum impregnation, and solution impregnation; see an example of vacuum impregnation in Fig. 7 [123]. Karaman et al. [124] prepared a PEG/diatomite composite PCM by using the vacuum impregnation method. The liquid PEG was infiltrated into the pores of the diatomite to form SSCPCM, reaching a maximum amount of PEG encapsulated into diatomite of up to 50 wt %. Li et al. [125] prepared a copper foam/SAT composite PCM by melt impregnation. To address the phase separation issue, a thickening agent, carboxymethyl cellulose (CMC), was used to increase the viscosity of SAT.

Nomura et al. [126] found that the geometry of the matrix was an important factor affecting both the impregnation ratio and the structure stability of the prepared SSCPCM. Goitandia et al. [127] investigated the confinement of PCMs in various matrices with different pore distributions, including EG, silica, bentonite, diatomite, and zeolite Y. It was found that matrices with a macroporous structure, e.g., EG and diatomite, presented more serious PCM leakage after 450 thermal cycles due to insufficient capillary force. Matrices with a microporous structure, e.g., zeolite with a pore size of ~0.6 nm and bentonite with a pore size of ~3.5 nm, also showed the leakage issue, which was because the PCM was mainly infiltrated into the

Table 5. Features of different species of matrices.

Matrix (T_{\max})	Polymeric matrix ($\sim 400^\circ\text{C}$)	Carbon matrix ($\sim 600^\circ\text{C}$)	Metallic matrix ($\sim 800^\circ\text{C}$)	Ceramic matrix (over 1000°C)
				
Advantages	chemically stable low cost durable	high thermal conductivity good chemical stability diverse sizes and geometries	high thermal conductivity high porosity high thermal stability great mechanical properties	high chemical stability excellent thermal stability low cost high surface energy and easy to be wetted
Disadvantages	low thermal conductivity flammability issues	high cost for nanosized carbon materials	high cost corrosion issue leakage issue for large pore size metal foam	not enough thermal conductivity for some ceramics

**Figure 7.** Preparation of PA/diatomite SSCPCM by vacuum impregnation (reproduced from [123] with permission from Wiley).

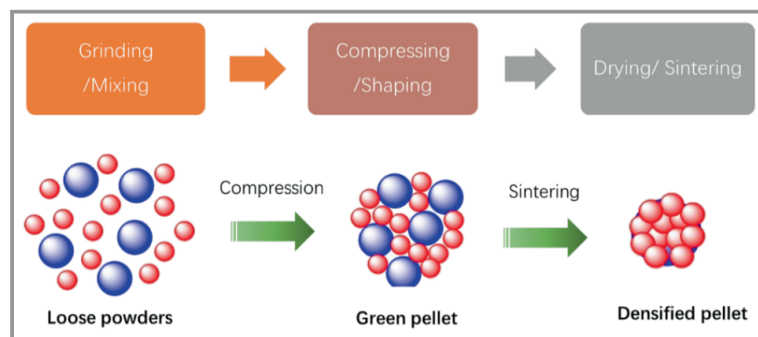
intergranular voids rather than the micropores. Among all matrices, mesoporous silica showed the lowest leakage. The above suggests an optimal impregnation ratio at which the infiltration into interparticle voids, and hence the associated leakage could be minimized.

3.3.2 Mix-Sintering Method

The mix-sintering method involves steps of grinding, mixing, shaping, drying, and sintering (see Fig. 8 for a schematic illustration). The raw materials, such as PCM, matrix, and property enhancers, are often ground to a specific particle size first. Then, they are mixed and compacted under high pressure into green pellets. The interparticle voids are significantly reduced during compression but cannot be removed completely. In the subsequent sintering step, the

PCM melts and starts to infiltrate into the pores of the matrix and also the interparticle voids, driven by the capillary force. In the meantime, the particles are rearranged gradually due to the attractive force created by the liquid. The rearrangement of the particles leads to the removal of some interparticle pores and hence to a densified structure [128].

Li et al. [129,130] prepared MgO-based SSCPCMs by mix-sintering and found that the particle size of the MgO matrix had a significant effect on the microstructure development and the thermophysical properties of the prepared SSCPCMs. Smaller MgO particles ($\sim 3\text{--}5\ \mu\text{m}$) were observed to contribute to a more compacted structure and thus a greater thermal conductivity and mechanical strength of the SSCPCM. Furthermore, SSCPCMs formulated with light MgO displayed a denser structure than the ones made with heavy MgO. Ge et al. prepared $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3/\text{MgO}$ SSCPCMs by the mix-sintering method [5,6]. They observed that a good wettability between the PCM and the matrix was essential to obtain a

**Figure 8.** Fabrication steps of the mix-sintering method (reproduced from [4] with permission from Elsevier).

stabilized structure. The good wetting behavior between PCM and matrix was also important to form a dense structure of the SSCPCM as the capillary force would pull the grains of the ceramic particles together to form a compacted structure. A low wettability was shown to create air gaps and thus form a porous structure in the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3/\text{graphite}$ system [131]. Jiang et al. [128] proposed a preheating process before compression, allowing the molten PCM to infiltrate into the porous matrix and/or the interparticle voids. The added preheating process led to a denser structure compared with the non-preheated SSCPCMs with an increase in density of $\sim 20\%$ and a decrease in porosity of $\sim 9.18\%$. They also indicated that a good wetting behavior between PCM and matrix was essential to obtain improvements with the preheating process as the capillary force plays an important role during particle compaction and rearrangement.

4 Particle Technology in Thermochemical Energy Storage Materials

Thermochemical energy storage (TCES) stores heat by reversible sorption and/or chemical reactions. TCES has a very high energy density with a volumetric energy density ~ 2 times that of latent heat storage materials, and 8–10 times that of sensible heat storage materials [132]. It is capable of long-term storage with little dissipation. TCES can be classified into sorption-based and chemical reaction-based categories. Examples of sorption-based TCES include liquid sorption, i.e., $\text{LiBr}/\text{H}_2\text{O}$ and $\text{LiCl}/\text{H}_2\text{O}$, and solid sorption, i.e., silica gel/ H_2O and zeolites/ H_2O , whereas examples of reversible reaction-based TCES include water

systems, e.g., $\text{MgSO}_4/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CaO}/\text{Ca}(\text{OH})_2$ pairs, carbon dioxide systems, e.g., CaO/CaCO_3 and SrO/SrCO_3 pairs, sulfate systems, e.g., MgO/MgSO_4 and CaO/CaSO_4 pairs, and redox systems, e.g., PbO/PbO_2 and BaO/BaO_2 pairs. The characteristics of these different types of TCES systems are shown in Tab. 6 [133].

Among these TCES materials, salt hydrates-water systems as working pairs have been intensively studied for mid- and low-temperature applications, owing to their cost-effectiveness, easy availability, non-toxicity, environmentally friendliness, and sound cyclability [134]. Despite the high energy density of thermochemical materials, low heat and mass transfer rates in the reactive bed often lead to their poor performance and low efficiency in practice. The degradation of TCES material structural integrity further deteriorates the heat and mass transfer. These, plus the strong hygroscopicity of the salt hydrates, present significant technical challenges in TCES-based TES technology [135].

4.1 Enhancement of Heat and Mass Transfer in TCES Materials

The incorporation of salt hydrates with particles or matrices can help stabilize their structure and prevent degradation during thermal cycling. The porous structure created by the particles or the matrix offers paths for mass transfer as well as the reaction process. Matrices with higher thermal conductivity, e.g., expanded graphite and CNTs, also facilitate the formation of a thermally conductive network, leading to an enhanced overall heat transfer. As a result, the selection of a host porous matrix is critical.

Table 6. Characteristics of different chemical reaction-based energy storage (reproduced from [133] with permission from the Royal Society of Chemistry).

Category	Chemical materials	Turnover temperature [°C]	Estimated storage energy density [GJ m^{-3}]
Water system (H_2O)	$\text{MgCl}_2/\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	130–150	2.5
	$\text{MgSO}_4/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	150	2.8
	$\text{CaCl}_2/\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	165–190	0.6
	$\text{MgO}_2/\text{Mg}(\text{OH})_2$	250–400	4.8
	$\text{CaO}_2/\text{Ca}(\text{OH})_2$	450–500	3.1
Carbon dioxide system (CO_2)	$\text{Li}_4\text{SiO}_4/\text{LiCO}_3 + \text{Li}_2\text{SiO}_3$	650–700	1.8
	CaO/CaCO_3	850	4.8
	SrO/SrCO_3	1200	5.9
Sulfate system (SOx)	MgO/MgSO_4	1080	6.2
	CaO/CaSO_3	1200–1250	8.7
Redox system (O_2)	PbO/PbO_2	292	2.0
	BaO/BaO_2	738	2.9
	$\text{CoO}/\text{Co}_3\text{O}_4$	925	5.0

The particles or matrices for enhancing the performance of TCES materials can be divided into inert and active categories, depending on whether the particles or matrices participate in thermochemical reactions. Exfoliated vermiculite (EV), expanded graphite (EG), and activated carbon foam (ACF) are often regarded as inert matrices that have been used to form salt hydrate composites due to their highly porous structure. Such inertness is relative as their porous structure also adsorbs water, but the associated heat effect is small compared with salt hydrates. Grekova et al. [136] impregnated vermiculite with LiCl to form composite TCES materials for both long-duration seasonal storage and short-duration daily storage applications. A mass ratio of 59 wt % salt was confined within the EV pores. The heat storage capacity of the prepared LiCl/vermiculite composite reached $2.3\text{--}2.6\text{ kJ g}^{-1}$ ($224\text{--}253\text{ kWh m}^{-3}$). Korhammer et al. [137] investigated approaches to address the low melting points, agglomeration, low cycle stability, and low sorption rates associated with CaCl_2 -based TCES. They found that the water uptake rate increased by 2 times by mixing CaCl_2 with KCl and loading the mixture to the pores of expanded natural graphite (ENG) and activated carbon foam (ACF). They also found that the TCES composites not only showed an improved cycle stability and water sorption performance, but also increased overall thermal conductivity. Palacios et al. [138] proposed the combination of TCES and PCM to form a “3 in 1 system” that stores sensible heat, latent heat and thermochemical heat in one system. The associated structure stability challenge is addressed by having one of the components act as the matrix for the other during charging/discharging (see Fig. 9).

Zeolite, silica gel, charcoals, and activated alumina are active host matrices [139]. These active matrix materials adsorb water, and hence act not only as a host but also as a TCES material. Whiting et al. [140] investigated the thermochemical performance of four zeolites incorporated with MgCl_2 and MgSO_4 . Their results showed that zeolites

impregnated with MgCl_2 showed a better performance than those with MgSO_4 , owing to less blockage of the pores and lower extent of deliquescence of MgCl_2 . They also found that Na-Y zeolite impregnated with 15 wt % MgCl_2 showed the best performance among all formulations investigated, due to high pore volume of Na-Y zeolite thus allowing a better water vapor transfer. Metal-organic frameworks (MOFs) are also a type of active matrix, which are made from metal nodes and organic molecules called linkers, with the organic linkers coordinating to the metal clusters to form micro- or mesoporous structures. D’Ans et al. [141] used mesoporous MIL-101(Cr) as a host to encapsulate SrBr_2 , and showed an overall heat storage density of 233 kWh m^{-3} . The composite was found to have an enhanced water sorption capacity compared to pure SrBr_2 or pure MOF. Tab. S2 of the Supporting Information summarizes the characteristics of several commonly used matrices for TCES materials.

4.2 Fabrication of TCES Composite Materials

The most popular method to incorporate a salt hydrate into a host matrix is dry, wet, or vacuum impregnation (see Fig. 10) [64]. The procedures of different impregnation methods are shown in Fig. 10. The key difference between dry impregnation and wet impregnation is the volume of salt solution versus pore volume. The dry impregnation method involves the use of a salt solution equal or slightly lower than the pore volume, while the volume of the salt solution exceeds the volume of the pores during wet impregnation. Due to the excess solution that cannot be absorbed by the pores, a portion of the salt covers the external surface [142]. After drying, such part of the salt can partially precipitate on the external surface of the particles [143, 144]. With dry impregnation, large grains of salts are rarely observed on the surface of the matrix.

The vacuum impregnation method uses vacuum to facilitate the impregnation process [145]. Mahon et al. [146] investigated two methods for the synthesis of $\text{MgSO}_4/13\text{X}$ molecular sieve composite, with one being the wet impregnation method and the other method was the compaction of a mixture of 13X molecular sieve powder and MgSO_4 to form composite pellets with a binder. Their results showed a poor hydration/dehydration performance due to blocked pores of 13X molecular sieve impregnated with MgSO_4 , whereas the composite pellets performed well.

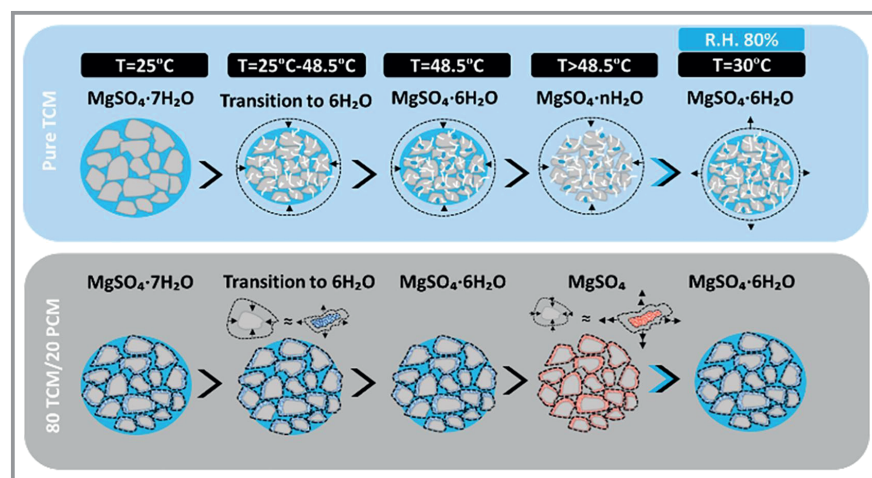


Figure 9. Pure TCM and TCM/PCM microstructure during dehydration and hydration (reproduced from [138] with permission from Elsevier).

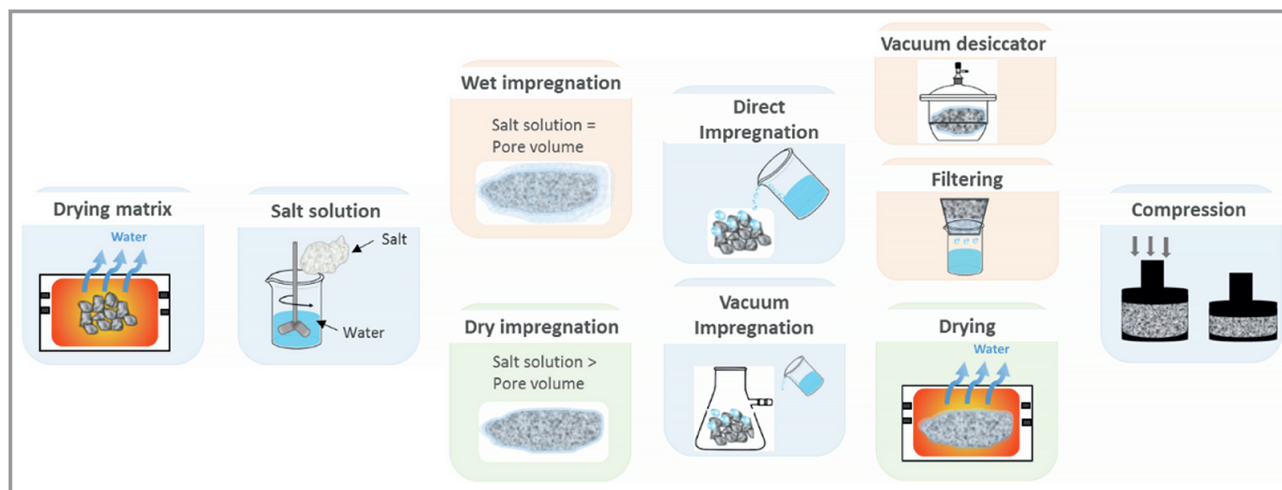


Figure 10. Impregnation methods scheme for TCES composite materials (reproduced from [64] with permission from the Royal Society of Chemistry).

5 Concluding Remarks

This article provides a state-of-art review of the formulation and fabrication of TES materials, covering sensible, latent, and thermochemical TES. The special focus is on the role of particle technology in the formulation, property enhancement, and manufacturing of these materials. Particle technology offers a way to address some of the key scientific and technological challenges of TES technologies, particularly those related to TES materials, including, e.g., low energy storage density, slow response speed, and life-span:

- The addition of doped nanoparticles in molten salt-based sensible TES materials could enhance their specific heat and thermal conductivity.
- The inclusion of property enhancers, e.g., particles and matrices, in latent heat storage materials can address the low thermal conductivity and supercooling of PCMs. The encapsulation of PCMs and structurally stabilized composite PCMs (SSPCMs) can effectively address leakage and chemical incompatibility challenges.
- The incorporation of an inert or an active host matrix into thermochemical TES materials can provide structural stabilization of the materials as well as mass transfer channels and effectively accommodate material swelling during thermal cycling.

In summary, particle technology has a pivotal role to play. Such a role ranges from the formulation and characterization to processing and manufacturing. Despite of significant progress in TES materials research, development, and deployment particularly over the last decade, significant challenges remain, and some examples are given in the following:

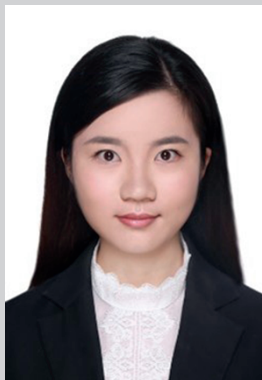
- sensible heat storage materials: low stability of nanoparticles in molten salts and lack of repeatability of property enhancement data

- latent heat storage materials: high supercooling of PCMs for cold energy storage, lack of PCMs for cryogenic temperature range (e.g., $-80\text{ }^{\circ}\text{C}$ and below), high costs of low- to medium-temperature PCMs (e.g., paraffin-based PCMs for heat storage below $\sim 100\text{ }^{\circ}\text{C}$ and PCMs for heat storage at $400\text{--}600\text{ }^{\circ}\text{C}$), insufficient life-span of some PCMs
- thermochemical storage materials: performance degradation and low life-span of most thermochemical storage materials

Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/cite.202200113>. This section includes additional references to primary literature relevant for this research [31–38, 42, 43, 45–51, 53–57, 59–62].

The authors acknowledge partial support of National Key R&D Program of China (No. 2018YFA0702300), Fundamental Research Funds for the Central Universities of China, and UK Engineering and Physical Sciences Research Council (EPSRC) under grant EP/V027050/1 (Industrial Decarbonisation Research and Innovation Centre – IDRIC).



Zhu Jiang is an associate professor at Southeast University, with more than 8 years of R&D experiences in thermal energy storage (TES) technology. Her research interests include formulation and microstructure regulation of phase change materials (15 °C to ~700 °C) and absorptive thermochemical materials, molten salt-based nanofluids and their corrosion behaviors, large-scale manufacturing techniques of advanced TES materials, hot-melt extrusion.



Xiaosong Zhang is the Director of Engineering Research Center for Building Energy Environment & Equipments (BEEE) at Southeast University. His research focuses on novel air conditioning systems (solution absorption-based) and efficient heat pumps, regulation of indoor humidity and temperature, solar energy utilization, energy-saving technologies in buildings.



Xinyi Li is a postgraduate student at Southeast University supervised by Prof. Dr. Zhu Jiang, who was previously graduated from Wuhan University of Science and Technology. Her research topic is on the formulation and microstructure regulation of highly oriented form-stable composite phase change materials and investigation on their characteristics.



Lige Tong is a professor at University of Science and Technology Beijing. Her research interests include energy conversion and efficient utilization, energy storage and management, high temperature flue gas dust removal and residual energy recycling, refrigeration and cryogenic engineering, service safety assessment of industrial equipment.



Yi Jin is the Chief Technology Officer of Jiangsu Jinhe Energy Technology Co., Ltd. He focuses on the large-scale deployment of thermal energy (heat and cold) storage systems, including large-scale production of thermal energy materials, efficient thermal energy storage devices and systems.



Li Wang is a professor at University of Science and Technology Beijing. His research covers energy conversion, storage, and utilization; air separation; refrigeration and cryogenics; new processes and technologies for energy conservation and emission reduction.



Yulong Ding is the founding Chamberlain Chair of Chemical Engineering and Director of University of Birmingham Centre for Energy Storage. His research in energy storage area includes liquid and compressed air energy storage and thermal energy storage based on molten salts, phase change materials, and thermochemical materials. He has published over 550 technical papers with ~400 in peer-reviewed journals (GS H Index of ~80) and filed ~100 patents.

Abbreviations

ACF	activated carbon foam
BN	boron nitride
BSE	backscattered electron
CF	carbon fiber
CMC	carboxymethyl cellulose
CSP	concentrating solar power
DLS	dynamic laser scanning
DSC	differential scanning calorimetry
EDX	energy-dispersive X-ray spectroscopy
EG	expanded graphite
ENG	expanded natural graphite
EV	exfoliated vermiculite
FSCPCM	form stable composite PCM
FT-IR	Fourier-transform infrared spectroscopy
GNP	graphene nanoplatelet
HTF	heat transfer fluid
LFA	laser flash analysis
LHS	latent heat storage
MF	malemine formaldehyde
MMA	methyl methacrylate
MOF	metal-organic frameworks
MWCNT	multi-wall carbon nanotube
NP	nanoparticle
PCM	phase change material
PEG	polyethylene glycol
PMMA	polymethyl methacrylate
SAT	sodium acetate trihydrate
SEM	scanning electron microscopy
SHS	sensible heat storage
SSCPCM	structurally stabilized composite PCM
TCES	thermochemical energy storage
TEM	transmission electron microscopy
TES	thermal energy storage
TGA	thermogravimetric analysis
XRD	X-ray diffraction

References

- [1] *Global Renewables Outlook Energy Transformation 2050*, International Renewable Energy Agency, Abu Dhabi **2020**.
- [2] *World Energy Transitions Outlook 2022: 1.5 °C Pathway*, International Renewable Energy Agency, Abu Dhabi **2022**.
- [3] P. G. Taylor, R. Bolton, D. Stone, P. Upham, *Energy Policy* **2013**, 63, 230–243. DOI: <https://doi.org/10.1016/j.enpol.2013.08.070>
- [4] Z. Jiang, A. Palacios, B. Zou, Y. Zhao, W. Deng, X. Zhang, Y. Ding, *Renewable Sustainable Energy Rev.* **2022**, 159, 112134. DOI: <https://doi.org/10.1016/j.rser.2022.112134>
- [5] Z. Ge, F. Ye, H. Cao, G. Leng, Y. Qin, *Particuology* **2014**, 15, 77–81. DOI: <https://doi.org/10.1016/j.PARTIC.2013.09.002>
- [6] Z. Ge, F. Ye, Y. Ding, *ChemSusChem* **2014**, 7 (5), 1318–1325. DOI: <https://doi.org/10.1002/CSSC.201300878>
- [7] O. Arthur, M. A. Karim, *Renewable Sustainable Energy Rev.* **2015**, 55, 739–755. DOI: <https://doi.org/10.1016/j.rser.2015.10.065>
- [8] D. Shin, D. Banerjee, *J. Heat Transfer* **2011**, 133 (2), 024501. DOI: <https://doi.org/10.1115/1.4002600>
- [9] M. Lasfargues, G. Stead, M. Amjad, Y. Ding, D. Wen, *Materials* **2017**, 10 (6), 537. DOI: <https://doi.org/10.3390/ma10050537>
- [10] D. Shin, D. Banerjee, *Int. J. Heat Mass Transfer* **2014**, 74, 210–214. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2014.02.066>
- [11] Y. Hu, Y. He, Z. Zhang, D. Wen, *Energy Convers. Manage.* **2017**, 142, 366–373. DOI: <https://doi.org/10.1016/j.enconman.2017.03.062>
- [12] M. Chieruzzi, G. F. Cerritelli, A. Miliozzi, J. M. Kenny, L. Torre, *Sol. Energy Mater. Sol. Cells* **2017**, 167, 60–69. DOI: <https://doi.org/10.1016/j.solmat.2017.04.011>
- [13] M. Lasfargues, A. Bell, Y. Ding, *J. Nanopart. Res.* **2016**, 18 (6), 150. DOI: <https://doi.org/10.1007/s11051-016-3460-8>
- [14] Q. Xie, Q. Zhu, Y. Li, *Nanoscale Res. Lett.* **2016**, 11 (1), 306. DOI: <https://doi.org/10.1186/s11671-016-1519-1>
- [15] Q. Yu, Y. Lu, X. Zhang, Y. Yang, C. Zhang, Y. Wu, *Sol. Energy Mater. Sol. Cells* **2021**, 230, 111215. DOI: <https://doi.org/10.1016/j.solmat.2021.111215>
- [16] A. Svobodova-Sedlackova, C. Barreneche, G. Alonso, A. I. Fernandez, P. Gamallo, *Renewable Energy* **2020**, 152, 208–216. DOI: <https://doi.org/10.1016/j.RENENE.2020.01.046>
- [17] D. Shin, D. Banerjee, *Int. J. Heat Mass Transfer* **2011**, 54 (5–6), 1064–1070. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2010.11.017>
- [18] S. M. M. Rizvi, B. El Far, D. Shin, *Int. J. Energy Res.* **2021**, 45 (4), 6350–6359. DOI: <https://doi.org/10.1002/ER.6148>
- [19] H. Tiznobaik, D. Shin, *Appl. Phys. Lett.* **2013**, 102 (17), 173906. DOI: <https://doi.org/10.1063/1.4801645>
- [20] H. Tiznobaik, D. Banerjee, D. Shin, *Int. J. Heat Mass Transfer* **2015**, 91, 342–346. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2015.05.072>
- [21] P. D. Myers Jr., T. E. Alam, R. Kamal, D. Y. Goswami, E. Stefanakos, *Appl. Energy* **2016**, 165, 225–233. DOI: <https://doi.org/10.1016/j.APENERGY.2015.11.045>
- [22] A. Awad, H. Navarro, Y. Ding, D. Wen, *Renewable Energy* **2018**, 120, 275–288. DOI: <https://doi.org/10.1016/j.RENENE.2017.12.026>
- [23] Y. Jin, J. Cheng, X. An, T. Su, P. Zhang, Z. Li, *Sol. Energy* **2016**, 137, 385–392. DOI: <https://doi.org/10.1016/j.solener.2016.08.037>
- [24] M. Lasfargues, H. Cao, Q. Geng, Y. Ding, *Materials* **2015**, 8 (8), 5194–5204. DOI: <https://doi.org/10.3390/ma8085194>
- [25] H. Chen, Y. Ding, Y. He, C. Tan, *Chem. Phys. Lett.* **2007**, 444 (4–6), 333–337. DOI: <https://doi.org/10.1016/J.CPLETT.2007.07.046>

- [26] B. Jo, D. Banerjee, *Mater. Lett.* **2014**, *122*, 212–215. DOI: <https://doi.org/10.1016/j.matlet.2014.02.032>
- [27] K. Skrbek, V. Bartůněk, D. Sedmidubský, *Renewable Sustainable Energy Rev.* **2022**, *164*, 112548. DOI: <https://doi.org/10.1016/j.rser.2022.112548>
- [28] B. El Far, S. M. M. Rizvi, Y. Nayfeh, D. Shin, *Int. J. Heat Mass Transfer* **2020**, *156*, 119789. DOI: <https://doi.org/10.1016/j.jheatmasstransfer.2020.119789>
- [29] B. El Far, S. M. M. Rizvi, Y. Nayfeh, D. Shin, *Sol. Energy Mater. Sol. Cells* **2020**, *210*, 110503. DOI: <https://doi.org/10.1016/j.solmat.2020.110503>
- [30] H. A. Aljaerani, M. Samykano, R. Saidur, A. K. Pandey, K. Kadirgama, *J. Energy Storage* **2021**, *44* (A), 103280. DOI: <https://doi.org/10.1016/j.est.2021.103280>
- [31] Z. Jiang, M. E. Navarro Rivero, X. Liu, X. She, Y. Xuan, Y. Ding, *Appl. Energy* **2021**, *303*, 117591. DOI: <https://doi.org/10.1016/J.APENERGY.2021.117591>
- [32] B. Muñoz-Sánchez, J. Nieto-Maestre, I. Iparraguirre-Torres, J. E. Julià, A. García-Romero, *AIP Conf. Proc.* **2017**, *1850*, 080018. DOI: <https://doi.org/10.1063/1.4984439>
- [33] B. Dudda, D. Shin, *Int. J. Therm. Sci.* **2013**, *69*, 37–42. DOI: <https://doi.org/10.1016/j.jthermalsci.2013.02.003>
- [34] H. Riaz, S. Mesgari, N. A. Ahmed, R. A. Taylor, *Int. J. Heat Mass Transfer* **2016**, *94*, 254–261. DOI: <https://doi.org/10.1016/j.jheatmasstransfer.2015.11.064>
- [35] Y. Hu, Y. He, Z. Zhang, D. Wen, *Sol. Energy Mater. Sol. Cells* **2019**, *192*, 94–102. DOI: <https://doi.org/10.1016/j.solmat.2018.12.019>
- [36] P. Andreu-Cabedo, R. Mondragon, L. Hernandez, R. Martinez-Cuenca, L. Cabedo, J. Julia, *Nanoscale Res. Lett.* **2014**, *9* (1), 582. DOI: <https://doi.org/10.1186/1556-276X-9-582>
- [37] M. Chieruzzi, G. F. Cerritelli, A. Miliuzzi, J. M. Kenny, *Nanoscale Res. Lett.* **2013**, *8* (1), 448. DOI: <https://doi.org/10.1186/1556-276X-8-448>
- [38] B. Muñoz-Sánchez et al., *Sol. Energy Mater. Sol. Cells* **2018**, *176*, 357–373. DOI: <https://doi.org/10.1016/j.solmat.2017.10.022>
- [39] M. Lasfargues, G. Stead, M. Amjad, Y. Ding, D. Wen, *Materials* **2017**, *10* (6), 537. DOI: <https://doi.org/10.3390/ma10050537>
- [40] M. Lasfargues, Q. Geng, H. Cao, Y. Ding, *Nanomaterials* **2015**, *5* (3), 1136–1146. DOI: <https://doi.org/10.3390/nano5031136>
- [41] Y. Luo, X. Du, A. Awad, D. Wen, *Int. J. Heat Mass Transfer* **2017**, *104*, 658–664. DOI: <https://doi.org/10.1016/j.jheatmasstransfer.2016.09.004>
- [42] U. Nithiyantham, L. González-Fernández, Y. Grosu, A. Zaki, J. M. Igartua, A. Faik, *Appl. Therm. Eng.* **2020**, *169*, 114942. DOI: <https://doi.org/10.1016/j.applthermaleng.2020.114942>
- [43] E. Hamdy, S. Ebrahim, F. Abulfotuh, M. Soliman, in *2016 Int. Renewable and Sustainable Energy Conf. (IRSEC)*, IEEE, New York **2016**, 317–320. DOI: <https://doi.org/10.1109/IRSEC.2016.7983997>
- [44] Y. Huang, X. Cheng, Y. Li, G. Yu, K. Xu, G. Li, *Sol. Energy* **2018**, *160*, 208–215. DOI: <https://doi.org/10.1016/j.solener.2017.11.077>
- [45] X. Wei, Y. Yin, B. Qin, W. Wang, J. Ding, J. Lu, *Renewable Energy* **2020**, *145*, 2435–2444. DOI: <https://doi.org/10.1016/j.renene.2019.04.153>
- [46] M. Schuller, Q. Shao, T. Lalk, *Int. J. Therm. Sci.* **2015**, *91*, 142–145. DOI: <https://doi.org/10.1016/j.jthermalsci.2015.01.012>
- [47] H. A. Aljaerani, M. Samykano, A. K. Pandey, K. Kadirgama, M. George, R. Saidur, *Int. Commun. Heat Mass Transfer* **2022**, *132*, 105898. DOI: <https://doi.org/10.1016/j.icheatmasstransfer.2022.105898>
- [48] J. Seo, D. Shin, *Micro Nano Lett.* **2014**, *9* (11), 817–820. DOI: <https://doi.org/10.1049/mnl.2014.0407>
- [49] J. Seo, D. Shin, *Appl. Therm. Eng.* **2016**, *102*, 144–148. DOI: <https://doi.org/10.1016/j.applthermaleng.2016.03.134>
- [50] Y. Ueki, N. Fujita, M. Kawai, M. Shibahara, *AIP Adv.* **2017**, *7* (5), 055117. DOI: <https://doi.org/10.1063/1.4984770>
- [51] X. Chen, Y. Wu, L. Zhang, X. Wang, C. Ma, *Sol. Energy Mater. Sol. Cells* **2018**, *176*, 42–48. DOI: <https://doi.org/10.1016/j.solmat.2017.11.021>
- [52] L. Zhang, X. Chen, Y. Wu, Y. Lu, C. Ma, *Sol. Energy Mater. Sol. Cells* **2016**, *157*, 808–813. DOI: <https://doi.org/10.1016/J.SOLMAT.2016.07.046>
- [53] M. Chieruzzi, A. Miliuzzi, T. Crescenzi, L. Torre, J. M. Kenny, *Nanoscale Res. Lett.* **2015**, *10* (1), 273. DOI: <https://doi.org/10.1186/s11671-015-0984-2>
- [54] G. Qiao, M. Lasfargues, A. Alexiadis, Y. Ding, *Appl. Therm. Eng.* **2017**, *111*, 1517–1522. DOI: <https://doi.org/10.1016/j.applthermaleng.2016.07.159>
- [55] D. Shin, D. Banerjee, *Int. J. Heat Mass Transfer* **2015**, *84*, 898–902. DOI: <https://doi.org/10.1016/j.jheatmasstransfer.2015.01.100>
- [56] H. Tiznobaik, D. Shin, *Int. J. Heat Mass Transfer* **2013**, *57* (2), 542–548. DOI: <https://doi.org/10.1016/j.jheatmasstransfer.2012.10.062>
- [57] B. Jo, D. Banerjee, *J. Heat Transfer* **2015**, *137* (9), 091013. DOI: <https://doi.org/10.1115/1.4030226>
- [58] Y. B. Tao, C. H. Lin, Y. L. He, *Energy Convers. Manage.* **2015**, *97*, 103–110. DOI: <https://doi.org/10.1016/J.ENCONMAN.2015.03.051>
- [59] F. Mortazavi, D. Banerjee, in *Proc. of the ASME 2016 Heat Transfer Summer Conf. collocated with the ASME 2016 Fluids Engineering Division Summer Meet. and the ASME 2016 14th Int. Conf. on Nanochannels, Microchannels, and Minichannels*, Vol. 1, The American Society of Mechanical Engineers, New York **2016**. DOI: <https://doi.org/10.1115/HT2016-7316>
- [60] N. A. C. Sidik, H. A. Mohammed, O. A. Alawi, S. Samion, *Int. Commun. Heat Mass Transfer* **2014**, *54*, 115–125. DOI: <https://doi.org/10.1016/j.icheatmasstransfer.2014.03.002>
- [61] S. M. M. Rizvi, D. Shin, *J. Energy Storage* **2021**, *43*, 103192. DOI: <https://doi.org/10.1016/j.est.2021.103192>
- [62] D. Han, B. G. Lougou, Y. Shuai, W. Wang, B. Jiang, E. Shagdar, *Sol. Energy Mater. Sol. Cells* **2022**, *234*, 111432. DOI: <https://doi.org/10.1016/j.solmat.2021.111432>
- [63] B. Munkhbayar, M. R. Tanshen, J. Jeoun, H. Chung, H. Jeong, *Ceram. Int.* **2013**, *39* (6), 6415–6425. DOI: <https://doi.org/10.1016/j.ceramint.2013.01.069>
- [64] M. E. Navarro, A. P. Trujillo, Z. Jiang, Y. Jin, Y. Zhang, Y. Ding, in *Thermal Energy Storage: Materials, Devices, Systems and Applications*, Royal Society of Chemistry, London **2021**.
- [65] B. Muñoz-Sánchez, J. Nieto-Maestre, I. Iparraguirre-Torres, A. García-Romero, J. M. Sala-Lizarraga, *Renewable Sustainable Energy Rev.* **2018**, *82*, 3924–3945. DOI: <https://doi.org/10.1016/J.RSER.2017.10.080>
- [66] M. Schuller, F. Little, D. Malik, M. Betts, Q. Shao, J. Luo, W. Zhong, S. Shankar, A. Padmanaban, *Molten Salt-Carbon Nanotube Thermal Energy Storage for Concentrating Solar Power Systems*, Final Report, Texas A&M University, College Station, TX **2012**. DOI: <https://doi.org/10.2172/1036948>
- [67] M. X. Ho, C. Pan, *Int. J. Heat Mass Transfer* **2014**, *70*, 174–184.
- [68] M. Johnsson, P. Pettersson, M. Nygren, *Thermochim. Acta* **1997**, *298* (1–2), 47–54. DOI: [https://doi.org/10.1016/S0040-6031\(97\)00206-2](https://doi.org/10.1016/S0040-6031(97)00206-2)
- [69] L. Liu, D. Su, Y. Tang, G. Fang, *Renewable Sustainable Energy Rev.* **2016**, *62*, 305–317. DOI: <https://doi.org/10.1016/j.rser.2016.04.057>

- [70] D. H. Choi, J. Lee, H. Hong, Y. T. Kang, *Int. J. Refrig.* **2014**, *42*, 112–120. DOI: <https://doi.org/10.1016/j.ijrefrig.2014.02.004>
- [71] W. Cui, Y. Yuan, L. Sun, X. Cao, X. Yang, *Renewable Energy* **2016**, *99*, 1029–1037. DOI: <https://doi.org/10.1016/J.RENENE.2016.08.001>
- [72] B. Tang, C. Wu, M. Qiu, X. Zhang, S. Zhang, *Mater. Chem. Phys.* **2014**, *144* (1–2), 162–167. DOI: <https://doi.org/10.1016/J.MATCHEMPHYS.2013.12.036>
- [73] T. Nomura, K. Tabuchi, C. Zhu, N. Sheng, S. Wang, T. Akiyama, *Appl. Energy* **2015**, *154*, 678–685. DOI: <https://doi.org/10.1016/j.apenergy.2015.05.042>
- [74] S. Harish, D. Orejon, Y. Takata, M. Kohno, *Appl. Therm. Eng.* **2017**, *114*, 1240–1246. DOI: <https://doi.org/10.1016/j.applthermaleng.2016.10.109>
- [75] X. Fang, L. W. Fan, Q. Ding, X. L. Yao, Y. Y. Wu, J. F. Hou, X. Wang, Z. T. Yu, G. H. Cheng, Y. C. Hu, *Energy Convers. Manage.* **2014**, *80*, 103–109. DOI: <https://doi.org/10.1016/j.enconman.2014.01.016>
- [76] P. Cheng, X. Chen, H. Gao, X. Zhang, Z. Tang, A. Li, G. Wang, *Nano Energy* **2021**, *85*, 105948. DOI: <https://doi.org/10.1016/J.NANOEN.2021.105948>
- [77] N. Sheng, T. Nomura, C. Zhu, H. Habazaki, T. Akiyama, *Sol. Energy Mater. Sol. Cells* **2019**, *192*, 8–15. DOI: <https://doi.org/10.1016/j.solmat.2018.12.018>
- [78] W. Wang, X. Yang, Y. Fang, J. Ding, J. Yan, *Appl. Energy* **2009**, *86* (7–8), 1196–1200. DOI: <https://doi.org/10.1016/j.apenergy.2008.10.020>
- [79] A. Hussain, C. Y. Tso, C. Y. H. Chao, *Energy* **2016**, *115*, 209–218. DOI: <https://doi.org/10.1016/j.energy.2016.09.008>
- [80] C. Wang, T. Lin, N. Li, H. Zheng, *Renewable Energy* **2016**, *96*, 960–965. DOI: <https://doi.org/10.1016/j.renene.2016.04.039>
- [81] W. Li, Y.-H. Wang, C.-C. Kong, *Int. Commun. Heat Mass Transfer* **2015**, *68*, 276–282. DOI: <https://doi.org/10.1016/J.ICHEATMASSTRANSFER.2015.09.004>
- [82] J. Wang, X. Jia, D. G. Atinafu, M. Wang, G. Wang, Y. Lu, *J. Mater. Chem. A* **2017**, *5* (46), 24321–24328. DOI: <https://doi.org/10.1039/c7ta05594c>
- [83] T. Wang, S. Wang, W. Wu, *Int. J. Heat Mass Transfer* **2017**, *109*, 930–937. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2017.02.068>
- [84] L. H. Li, E. J. G. Santos, T. Xing, E. Cappelluti, R. Roldán, Y. Chen, K. Watanabe, T. Taniguchi, *Nano Lett.* **2015**, *15* (1), 218–223. DOI: <https://doi.org/10.1021/nl503411a>
- [85] J. Hu, Y. Huang, Y. Yao, G. Pan, J. Sun, X. Zeng, R. Sun, J. Bin Xu, B. Song, C. P. Wong, *ACS Appl. Mater. Interfaces* **2017**, *9* (15), 13544–13553. DOI: <https://doi.org/10.1021/acsami.7b02410>
- [86] I. Shamseddine, F. Pennec, P. Biwole, F. Fardoun, *Renewable Sustainable Energy Rev.* **2022**, *158*, 112172. DOI: <https://doi.org/10.1016/J.RSER.2022.112172>
- [87] G. A. Lane, *Sol. Energy Mater. Sol. Cells* **1992**, *27* (2), 135–160. DOI: [https://doi.org/10.1016/0927-0248\(92\)90116-7](https://doi.org/10.1016/0927-0248(92)90116-7)
- [88] N. Xie, Z. Huang, Z. Luo, X. Gao, Y. Fang, Z. Zhang, *Appl. Sci.* **2017**, *7* (12), 1317. DOI: <https://doi.org/10.3390/APP7121317>
- [89] G. Feng, X. Xu, N. He, H. Li, K. Huang, *Mater. Res. Innovations* **2015**, *19* (S5), S5-972–S5-977. DOI: <https://doi.org/10.1179/1432891714Z.0000000001232>
- [90] X. Li, Y. Zhou, H. Nian, X. Ren, O. Dong, C. Hai, Y. Shen, J. Zeng, *Appl. Therm. Eng.* **2016**, *102*, 38–44. DOI: <https://doi.org/10.1016/J.APPLTHERMALENG.2016.03.098>
- [91] B. Yang, N. Wang, Y. Song, J. Liu, *Renewable Energy* **2021**, *175*, 80–97. DOI: <https://doi.org/10.1016/J.RENENE.2021.04.125>
- [92] X. Wu, Y. Wang, R. Sun, M. Lai, R. Du, Z. Zhang, *J. Phys.: Conf. Ser.* **2009**, *188* (1), 012046. DOI: <https://doi.org/10.1088/1742-6596/188/1/012046>
- [93] X. Li, Y. Zhou, H. Nian, X. Zhang, O. Dong, X. Ren, J. Zeng, C. Hai, Y. Shen, *Energy Fuels* **2017**, *31* (6), 6560–6567. DOI: <https://doi.org/10.1021/ACS.ENERGYFUELS.7B00851>
- [94] X. Zhang, Y. Fan, X. Tao, K. Yick, *J. Colloid Interface Sci.* **2005**, *281* (2), 299–306. DOI: <https://doi.org/10.1016/J.JCIS.2004.08.046>
- [95] L. Chai, X. Wang, D. Wu, *Appl. Energy* **2015**, *138*, 661–674. DOI: <https://doi.org/10.1016/J.APENERGY.2014.11.006>
- [96] H. Zhang, X. Wang, D. Wu, *J. Colloid Interface Sci.* **2010**, *343* (1), 246–255. DOI: <https://doi.org/10.1016/J.JCIS.2009.11.036>
- [97] K. Yuan, H. Wang, J. Liu, X. Fang, Z. Zhang, *Sol. Energy Mater. Sol. Cells* **2015**, *143*, 29–37. DOI: <https://doi.org/10.1016/J.SOLMAT.2015.06.034>
- [98] L. C. Chow, J. K. Zhong, J. E. Beam, *Int. Commun. Heat Mass Transfer* **1996**, *23* (1), 91–100. DOI: [https://doi.org/10.1016/0735-1933\(95\)00087-9](https://doi.org/10.1016/0735-1933(95)00087-9)
- [99] Y. Shin, D.-I. Yoo, K. Son, *J. Appl. Polym. Sci.* **2005**, *96* (6), 2005–2010. DOI: <https://doi.org/10.1002/APP.21438>
- [100] E. Y. Kim, H. D. Kim, *J. Appl. Polym. Sci.* **2005**, *96* (5), 1596–1604. DOI: <https://doi.org/10.1002/APP.21603>
- [101] W. Zhao, Y. Zheng, J. C. Sabol, K. Tuzla, S. Neti, A. Oztekin, J. C. Chen, *Renewable Energy* **2013**, *50*, 988–993. DOI: <https://doi.org/10.1016/J.RENENE.2012.08.036>
- [102] Y. Zheng, W. Zhao, J. C. Sabol, K. Tuzla, S. Neti, A. Oztekin, J. C. Chen, *Sol. Energy* **2013**, *87* (1), 117–126. DOI: <https://doi.org/10.1016/J.SOLENER.2012.10.003>
- [103] R. Jacob, F. Bruno, *Renewable Sustainable Energy Rev.* **2015**, *48*, 79–87. DOI: <https://doi.org/10.1016/J.RSER.2015.03.038>
- [104] Y. Yamagishi, T. Sugeno, T. Ishige, H. Takeuchi, A. T. Pyatenko, in *IECEC 96. Proc. of the 31st Intersociety Energy Conversion Engineering Conf.*, Vol. 3, IEEE, New York **2002**.
- [105] S. Tahan Latibari, M. Mehrali, M. Mehrali, T. M. Indra Mahlia, H. S. Cornelis Metselaar, *Energy* **2013**, *61*, 664–672. DOI: <https://doi.org/10.1016/J.ENERGY.2013.09.012>
- [106] J. Giro-Paloma, M. Martínez, L. F. Cabeza, A. I. Fernández, *Renewable Sustainable Energy Rev.* **2016**, *53*, 1059–1075. DOI: <https://doi.org/10.1016/J.RSER.2015.09.040>
- [107] H. Liu, X. Wang, D. Wu, *Sustainable Energy Fuels* **2019**, *3* (5), 1091–1149. DOI: <https://doi.org/10.1039/c9se00019d>
- [108] J. Shi, X. Wu, R. Sun, B. Ban, J. Li, J. Chen, *Colloids Surf.* **2019**, *571*, 36–43. DOI: <https://doi.org/10.1016/J.COLSURFA.2019.03.029>
- [109] C. Li, H. Yu, Y. Song, H. Liang, X. Yan, *Energy* **2019**, *167*, 1031–1039. DOI: <https://doi.org/10.1016/J.ENERGY.2018.11.038>
- [110] G. V. Belessiotis, K. G. Papadokostaki, E. P. Favvas, E. K. Efthimiadou, S. Karellas, *Energy Convers. Manage.* **2018**, *168*, 382–394. DOI: <https://doi.org/10.1016/J.ENCONMAN.2018.04.059>
- [111] T. Nomura, C. Zhu, N. Sheng, G. Saito, T. Akiyama, *Sci. Rep.* **2015**, *5* (1), 9117. DOI: <https://doi.org/10.1038/SREP09117>
- [112] J. Li, W. Lu, Z. Luo, Y. Zeng, *Sol. Energy Mater. Sol. Cells* **2017**, *159*, 440–446. DOI: <https://doi.org/10.1016/J.SOLMAT.2016.09.051>
- [113] M. D. Romero-Sanchez, R. R. Piticescu, A. M. Motoc, F. Aran-Ais, A. I. Tudor, *Manuf. Rev.* **2018**, *5*, 8. DOI: <https://doi.org/10.1051/MFREVUEW/2018003>
- [114] F. Rodríguez-Cumplido, E. Pabón-Gelves, F. Chejne-Jana, *J. Energy Storage* **2019**, *24*, 100821. DOI: <https://doi.org/10.1016/J.JEST.2019.100821>
- [115] A. Jamekhorshid, S. M. Sadrameli, M. Farid, *Renewable Sustainable Energy Rev.* **2014**, *31*, 531–542. DOI: <https://doi.org/10.1016/J.RSER.2013.12.033>
- [116] S. Drissi, T.-C. Ling, K. H. Mo, A. Eddhahak, *Renewable Sustainable Energy Rev.* **2019**, *110*, 467–484. DOI: <https://doi.org/10.1016/J.RSER.2019.04.072>

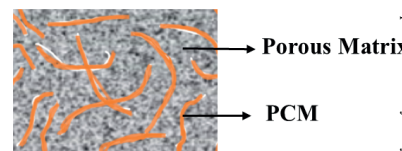
- [117] H. Gao, J. Wang, X. Chen, G. Wang, X. Huang, A. Li, W. Dong, *Nano Energy* **2018**, *53*, 769–797. DOI: <https://doi.org/10.1016/j.nanoen.2018.09.007>
- [118] R. Liu, F. Zhang, W. Su, H. Zhao, C. Wang, *Sol. Energy Mater. Sol. Cells* **2015**, *134*, 268–274. DOI: <https://doi.org/10.1016/J.SOLMAT.2014.12.012>
- [119] I. Sarbu, C. Sebarchievici, I. Sarbu, C. Sebarchievici, *Sustainability* **2018**, *10* (2), 191. DOI: <https://doi.org/10.3390/su10010191>
- [120] Y. Qin, G. Leng, X. Yu, H. Cao, G. Qiao, Y. Dai, Y. Zhang, Y. Ding, *Powder Technol.* **2015**, *282*, 37–42. DOI: <https://doi.org/10.1016/j.powtec.2014.08.075>
- [121] Y. Qin, X. Yu, G. H. Leng, L. Zhang, Y. L. Ding, *Mater. Res. Innovations* **2014**, *18* (2), 453–456. DOI: <https://doi.org/10.1179/1432891714Z.0000000000449>
- [122] S. Manan, J. Pitroda, J. J. Bhavsar, in *Int. Conf. on "Engineering: Issues, Opportunities and Challenges for Development"*, Bardoli, India, April **2015**.
- [123] W. Jia, C. Wang, T. Wang, Z. Cai, K. Chen, *Int. J. Energy Res.* **2020**, *44* (6), 4298–4308. DOI: <https://doi.org/10.1002/ER.5197>
- [124] S. Karaman, A. Karaipekli, A. Sari, A. Biçer, *Sol. Energy Mater. Sol. Cells* **2011**, *95* (7), 1647–1653. DOI: <https://doi.org/10.1016/j.solmat.2011.01.022>
- [125] T. X. Li, D. L. Wu, F. He, R. Z. Wang, *Int. J. Heat Mass Transfer* **2017**, *115*, 148–157. DOI: <https://doi.org/10.1016/j.ijheatmasstransfer.2017.07.056>
- [126] T. Nomura, N. Okinaka, T. Akiyama, *Mater. Chem. Phys.* **2009**, *115*, 846–850. DOI: <https://doi.org/10.1016/j.matchemphys.2009.02.045>
- [127] A. M. Goitandia, G. Beobide, E. Aranzabe, A. Aranzabe, *Sol. Energy Mater. Sol. Cells* **2015**, *134*, 318–328. DOI: <https://doi.org/10.1016/J.SOLMAT.2014.12.010>
- [128] Z. Jiang, M. E. Navarro Rivero, A. Anagnostopoulos, X. She, X. Liu, Y. Xuan, Y. Ding, *Powder Technol.* **2021**, *391*, 544–556. DOI: <https://doi.org/10.1016/J.POWTEC.2021.06.030>
- [129] C. Li, Q. Li, L. Cong, F. Jiang, Y. Zhao, C. Liu, Y. Xiong, C. Chang, Y. Ding, *Appl. Energy* **2019**, *250*, 81–91. DOI: <https://doi.org/10.1016/J.APENERGY.2019.04.094>
- [130] C. Li, Q. Li, L. Cong, Y. Li, X. Liu, Y. Xuan, Y. Ding, *Sol. Energy Mater. Sol. Cells* **2019**, *196*, 25–35. DOI: <https://doi.org/10.1016/J.SOLMAT.2019.03.035>
- [131] A. Anagnostopoulos, H. Navarro, A. Alexiadis, Y. Ding, *J. Phys. Chem. C* **2020**, *124* (15), 8140–8152. DOI: <https://doi.org/10.1021/acs.jpcc.0c00978>
- [132] D. Aydin, S. P. Casey, S. Riffat, *Renewable Sustainable Energy Rev.* **2015**, *41*, 356–367. DOI: <https://doi.org/10.1016/J.RSER.2014.08.054>
- [133] S. T. Kim, H. Takasu, Y. Kato, in *Thermal Energy Storage: Materials, Devices, Systems and Applications*, Royal Society of Chemistry, London **2021**.
- [134] H. Liu, W. Wang, Y. Zhang, *J. Cleaner Prod.* **2021**, *313*, 127908. DOI: <https://doi.org/10.1016/J.JCLEPRO.2021.127908>
- [135] J. Lin, Q. Zhao, H. Huang, H. Mao, Y. Liu, Y. Xiao, *Sol. Energy* **2021**, *214*, 149–178. DOI: <https://doi.org/10.1016/J.SOL-ENER.2020.11.055>
- [136] A. D. Grekova, L. G. Gordeeva, Y. I. Aristov, *Appl. Therm. Eng.* **2017**, *124*, 1401–1408. DOI: <https://doi.org/10.1016/J.APPLTHERMALENG.2017.06.122>
- [137] K. Korhammer, M. M. Druske, A. Fopah-Lele, H. U. Rammelberg, N. Wegscheider, O. Opel, T. Osterland, W. Ruck, *Appl. Energy* **2016**, *162*, 1462–1472. DOI: <https://doi.org/10.1016/J.APENERGY.2015.08.037>
- [138] A. Palacios, M. Elena Navarro, C. Barreneche, Y. Ding, *Appl. Energy* **2020**, *274*, 115024. DOI: <https://doi.org/10.1016/J.APENERGY.2020.115024>
- [139] R. J. Clark, A. Mehrabadi, M. Farid, *J. Energy Storage* **2020**, *27*, 101145. DOI: <https://doi.org/10.1016/J.EST.2019.101145>
- [140] G. Whiting, D. Grondin, S. Bennici, A. Auroux, *Sol. Energy Mater. Sol. Cells* **2013**, *112*, 112–119. DOI: <https://doi.org/10.1016/J.SOLMAT.2013.01.020>
- [141] P. D'Ans, E. Courbon, A. Permyakova, F. Nouar, C. Simonnet-Jégat, F. Bourdreux, L. Malet, C. Serre, M. Frère, N. Steunou, *J. Energy Storage* **2019**, *25*, 100881. DOI: <https://doi.org/10.1016/J.EST.2019.100881>
- [142] L. G. Gordeeva, A. Freni, T. A. Krieger, G. Restuccia, Y. I. Aristov, *Microporous Mesoporous Mater.* **2008**, *112* (1–3), 254–261. DOI: <https://doi.org/10.1016/j.micromeso.2007.09.040>
- [143] H. Jarimi, D. Aydin, Z. Yanan, G. Ozankaya, X. Chen, S. Riffat, *Int. J. Low-Carbon Technol.* **2019**, *14* (1), 44–69. DOI: <https://doi.org/10.1093/ijlct/cty052>
- [144] L. X. Gong, R. Z. Wang, Z. Z. Xia, C. J. Chen, *J. Chem. Eng. Data* **2010**, *55* (8), 2920–2923. DOI: <https://doi.org/10.1021/jc900993a>
- [145] L. G. Gordeeva, Y. I. Aristov, *Int. J. Low-Carbon Technol.* **2012**, *7* (4), 288–302. DOI: <https://doi.org/10.1093/ijlct/cts050>
- [146] D. Mahon, G. Claudio, P. C. Eames, *Energy Convers. Manage.* **2017**, *150*, 870–877. DOI: <https://doi.org/10.1016/J.ENCONMAN.2017.03.080>

DOI: 10.1002/cite.202200113

Particle Technology in the Formulation and Fabrication of Thermal Energy Storage Materials

Zhu Jiang, Xinyi Li, Yi Jin, Xiaosong Zhang, Lige Tong, Li Wang, Yulong Ding*

Review Article: Globally, more than 50 % of final energy consumption is thermal energy. Therefore, cost-effective and flexible thermal energy storage (TES) technologies will play a significant role in future zero-carbon energy systems. This review gives an overview of the state of the art in the formulation and fabrication of TES materials with focus on particle technology.



Supporting Information
available online