

Composite phase change materials for thermal energy storage

Li, Chuan; Li, Qi; Zhao, Yanqi; Cong, Lin; Jiang, Zhu; Li, Yongliang; Ding, Yulong

DOI:

[10.1016/j.egypro.2019.01.760](https://doi.org/10.1016/j.egypro.2019.01.760)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Li, C, Li, Q, Zhao, Y, Cong, L, Jiang, Z, Li, Y & Ding, Y 2019, 'Composite phase change materials for thermal energy storage: From molecular modelling based formulation to innovative manufacture', *Energy Procedia*, vol. 158, pp. 4510-4516. <https://doi.org/10.1016/j.egypro.2019.01.760>

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

Publisher Rights Statement:

Checked for eligibility: 23/05/2019

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.



Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 158 (2019) 4510–4516

Energy

Procedia

www.elsevier.com/locate/procedia

10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Composite phase change materials for thermal energy storage: From molecular modelling based formulation to innovative manufacture

Chuan Li, Qi Li, Yanqi Zhao, Lin Cong, Zhu Jiang, Yongliang Li, Yulong Ding*

Birmingham Centre for Energy Storage (BCES) & School of Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, UK

Abstract

Thermal energy storage (TES) has a crucial role to play in conserving and efficiently utilising energy, dealing with mismatch between demand and supply, and enhancing the performance and reliability of our current energy systems. A competitive TES technology requires a number of scientific and technological challenges to be addressed including TES materials, TES components and devices, and integration of TES devices with energy networks and associated dynamic optimization. This paper concerns mainly about TES materials challenges with a specific focus on using shape stable composite phase change materials (CPCMs) for medium and high temperature application. The paper first briefly reviews the state-of-the-art development of materials research for thermal energy storage. The focus is then on CPCMs for medium to high temperatures applications, covering materials screening, formulation based on molecular modelling validated at a different length scale through experiments, formulation based on chemical and physical compatibility, and manufacture of material modules via innovative use of conventional powder technology. The properties of the materials and materials modules are characterised and analysed with an aim to establish property-structure relationships. This includes a particularly interesting aspect of the motion of PCM and nanoscale objects with the PCMs for heat transfer enhancement during thermal cycling, which explains the mechanisms of the encapsulation of PCMs in the composite.

© 2019 The Authors. Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: Composite phase change materials; Thermal energy storage; Microstructural characteristics; Manufacture; Medium and high temperature

* Corresponding author. Tel.: +44-121-414-5279

E-mail address: y.ding@bham.ac.uk

1876-6102 © 2019 The Authors. Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.
10.1016/j.egypro.2019.01.760

1. Introduction

Thermal energy storage (TES) relates to a collection of technologies that store excessive energy in the forms of heat, cold and their combination in a medium termed TES material, and utilizes the stored thermal energy either directly or indirectly through energy conversion process when needed. TES currently accounts for approximately 55% of global non-pumped hydro installations [1-5]. Medium and high temperature TES has been widely applied in industrial waste heat recovery, solar thermal power generation and peak load shifting of electric power [6-8]. TES for waste heat recovery can solve the problem of matching the discontinuous heat source supply with the heat demand achieving a better capacity factor, allowing the process components to be designed for a lower maximum output hence reducing the investment cost [5]. As it can be seen in Table 1, there is wide waste energy sources related with metal and mineral industry (medium-high temperature) as well as food and tobacco processing sectors [9].

Table 1. Working temperatures of different industries where TES technologies can be applied

Industry	Working Temperatures (C)
iron- and steelmaking	1450–1550
Steel electric arc furnace	1370–1650
Aluminium furnace	1100–1200
Cooper refining furnace	760–820
Mineral Processing	150-1000
Glass	600-800
Chemicals	95-300
Paper industry	50-120
Food Industry	30-150

A competitive TES technology requires a number of scientific and technological challenges to be overcome including TES materials, TES components and devices, and integration of TES devices with energy networks and associated dynamic optimization. For TES materials, the challenges are associated with improving the properties including energy storage density, thermal conductivity, lifespan, operation temperature range and mechanical strength under larger temperature swings as well as cost reduction [6]. The use of microstructured composite phase change materials (CPCMs) provides an effective way to meet these challenges. Such CPCMs commonly consist of a PCM, a ceramic skeleton material (CSM) and a thermal conductivity enhancement material (TCEM) [9]. A right combination of these different ingredients could give a hierarchical structure that is able to encapsulate the PCM and give a substantial enhancement in the thermal conductivity. The scope of this paper is to give an overview on the development of medium and high temperature composite PCMs research for TES. In order to produce and manufacture TES materials for TES a thoughtfully scale up process has to be followed to adapt and maximize the performance according to the application. Firstly it has to be considered the selection of the material and then the thermal performance enhancement of itself. Moreover, the mechanism between the structure and performance are analysed at different length scales. Furthermore, the manufacturing process is taking into account for large scale applications. This includes a particularly interesting aspect of the motion of PCM and nanoscale objects with the PCM for heat transfer enhancement during thermal cycling, which explains the mechanisms of the encapsulation of PCMs in the composite.

2. Phase change materials (PCMs)

The PCMs are gaining increasing attention in recent years due to their high energy density and ability to store and release heat at a constant temperature during phase change. Numerous PCMs have proposed and studied in the literature. These materials can be divided into three groups of solid-solid PCMs, solid-liquid PCMs and liquid-gas

PCMs. Solid-liquid phase change processes normally give a small change of volume and relatively high latent heat, and are therefore broadly recognized and widely used. Solid-liquid PCMs can be further classified into three main categories of inorganic, organic and eutectic PCMs. Inorganic PCMs include salt hydrates, salt composites and metallics. Organic PCMs consists of paraffins and non-paraffins such as fatty acids, esters and alcohols. Eutectic PCMs are made of two or more components, which can be organic-organic, inorganic-inorganic and inorganic-organic combinations. These PCMs differ in not only the melting temperature and thermal properties, but also in melting-solidification process and are hence present various issues: organic PCMs and salt hydrates suffer from phase segregation and sub-cooling; inorganic PCMs have a low thermal conductivity and segregation; Eutectic PCMs and molten salts are corrosive [2, 4]. Various approaches have been proposed to resolve these problems particularly for organic materials and inorganic hydrates [9]. These include encapsulation of PCMs to reduce sub-cooling and overcome leakage, and addition of highly thermally conductive materials such as metal foams and carbon materials to enhance their thermal conductivity [3]. However, these methods are not effective for molten salt based PCMs due to low thermal conductivity as well as chemical incompatibility [4]. Recent research has indicated that the use of CPCMs could provide an effective avenue to resolve these problems. Here, the CPCMs usually consist of a PCM, a TCEM and a CSM for shape stabilization. Such a combination has been shown to give an excellent combination of energy density, power density and mechanical properties [2]. A right combination of these three chemically and physically compatible ingredients could give a hierarchical structure that is able to encapsulate the PCM and give a substantial enhancement in the thermal conductivity. Understanding of the structure-property relationships for the composites is therefore essential for the formulation design and manufacture of the materials.

3. Composite phase change materials (CPCMs) formulation

3.1 Materials selection

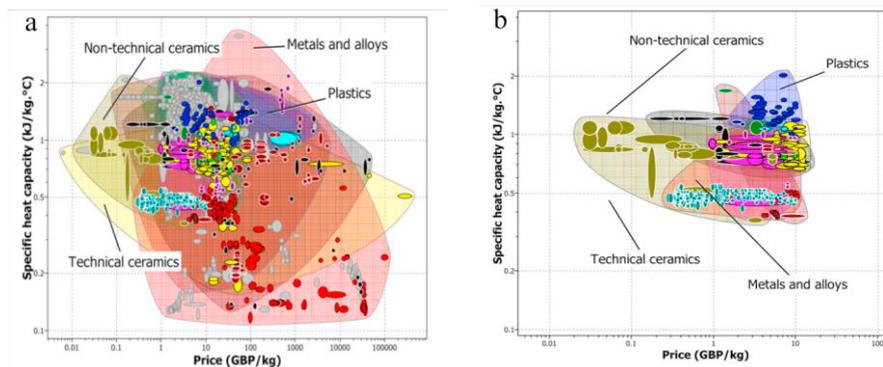


Fig. 1. Materials selection according to temperature application and energy density. (a) 220 °C minimum working temperatures. (b) 10£/kg maximum price constrain.

Materials selection is the primary step for the CPCMs formulation in order to choose a material for a specific application meeting at the same time specific requirements do to the materials performance often being a compromise between materials properties while minimizing the cost. It is based first on the identification of the most relevant thermophysical properties, in the case of TES that means a high latent heat and a suitable melting point followed by a good thermal conductivity. Thermal conductivity is taking into account the importance on charging/discharging times. Other properties such as thermal inertia, space or weight constrains and chemical compatibility and cost will depend on the final application, as well as other relevant issues regarding to durability, safety, environmental impact, etc. As mentioned above, PCMs can store high amounts of energy and release it when it is needed at a constant temperature, being in that case the most important property in selection materials the energy density. Given the amount and growing number of new materials being researched nowadays finding the optimal material became a complicated and time consuming process. Vitorino et al. [11] categorised the PCM in low

temperature range below 220 °C, medium range up to 420 °C, and high range greater than 420 °C. In their studies a preselection was done in order to apply the working conditions that constrain the materials suitable to be candidates. For medium and high temperature applications, according to the above classification, a minimum working temperature of 220 °C is selected as a key constrain. As it can be seen in Fig. 1a, major part of polymeric materials are discarded as well as organic ones because they present chemical changes such as oxidation above 220 °C. The materials chosen can be then considered into molten salts and metals. Metals present high thermal conductivity that assures a low charge/discharge process. However, comparing to polymers and molten salts the price is much higher making them less competitive when there are no other constraints such as available space and fast delivery time (see Fig. 1b).

3.2 Formulation based on molecular scale modelling

In order to improve the thermal performance of the molten salts and avoid or minimize the corrosion due to its utilizations, several approaches have been proposed. Specific heat capacity improvement has been done through the addition of nanoparticles while the thermal conductivity enhancement has been achieved by the introduction into the formulation of highly conductive materials such as metallic fins, foams, wools or different particle size materials such as nanoparticles.

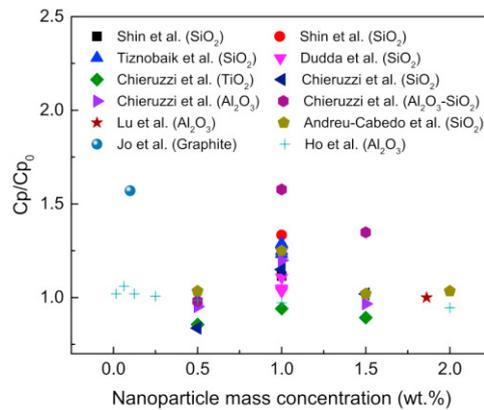


Fig. 2. The C_p/C_{p0} in molten salt based nanofluids

The improve of thermal performance of molten salts due to the anomalous high specific heat capacity has been extensively studied since it was observed. A prominent breakthrough that can improve the energy density with adequate and cost-effective means is in great need. All results in the literatures are summarized in Fig. 2. Most data have shown an increase tendency which suggests that the mechanism of the specific heat capacity cannot be simply explained by any of the current existing models or theories. There are several new theories proposed in the literatures. Shin and Banerjee [12] proposed three independent competing inter-molecular interaction mechanisms, suggesting that the higher specific heat capacity of nanofluids could be attributed to the higher specific heat capacity of nanoparticles which have a high surface energy. Molecular Dynamic (MD) simulations and experiments have been used to study the thermal properties obtained after the incorporation of nanoparticles. Based on the experimental and simulations results, Jo and Banerjee [13] suggested that the introduction of nanoparticles might be capable of changing the local molar composition of the salt based fluid, owing to the formation of the compressed liquid layer on the surface of nanoparticles. Qiao et al. [14] proposed a model for MD simulation that for the first time supported two of the existing theories, the existence of a semi-solid molecules adhering to the surface of a nanoparticle and the enhancement was due to the reduced inter-molecular spacing and semi-solid behaviour of this layer.

3.3 CPCMs manufacture

Early studies for the manufacture of CPCMs started at low temperature applications. For medium and high temperature applications, as mentioned before, the available materials are reduced and the selection of the proper materials to avoid chemical stability and incompatibilities are challenging. The cold compression and sintering method has been shown to be suitable for making CPCM for medium to high temperature applications. Fig. 3 shows the detailed procedure. One can see that, the CPCM usually contains three ingredients of a PCM to store and release latent heat, a supporting material to form structural skeleton, and an additive to enhance thermal properties. These raw materials are mixed and grinded into uniform particles. Particle size which may affect the density of the composite should be controlled in the manufacturing process. Sometimes some binders can be added into the mixture to bind the particles closely, which can help to form skeleton of the composite. Upon compressing, the void space between particles has been reduced significantly leading to an increase in the green composite. After sintering, the melting liquid provides a tension to gather the grains of skeleton material and bonds them together, which result in a densified composite with a relatively high rigidity and high thermal conductivity.

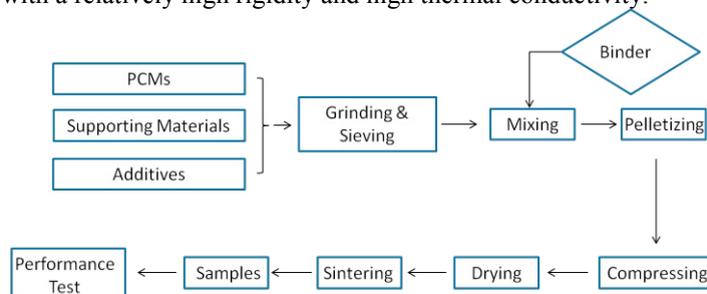


Fig. 3. Schematic diagrams of cold compression and sintering method

4. Structure-property relationships and microstructure characterization

Understanding the microstructural characteristics is essential for the establishment of structure-property relationship for CPCMs and hence the capability of design and manufacture of the material. In this section a typical MgO based carbonate salt CPCMs was used which are mainly for the medium and high temperature TES applications. The goal is to study the microstructure characteristics and structural changes during thermal cycles. A eutectic molten salt with a composition of 50 wt.% of Li_2CO_3 and 50 wt.% Na_2CO_3 has been selected as PCM. MgO and natural graphite flake were used as the CSM and TCEM, respectively. The cold compression and sintering manufacturing process has been selected. Fig. 4 shows SEM images of the composites containing graphite. A layered structure is observed in composite and which is due to the addition of graphite flakes and the flat surface of the graphite particles orientate perpendicularly to the compression force. Fig. 4 also shows a graphite rich area and there micro-gaps between graphite flakes and other ingredients in the composites. This could be attributed to the poor wettability of salt on graphite [2-4]. An inspection of Fig. 4(a) suggests the formation of a molten salt liquefied structure (MSLS) within the composites, leading to a dense structure.

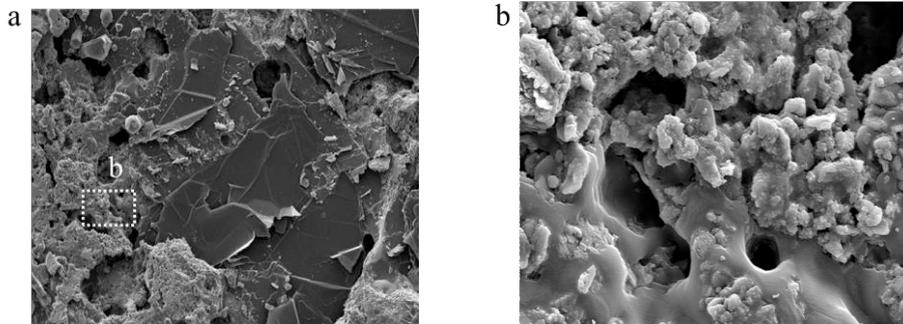


Fig. 4. SEM images of sintered NaLiCO₃-MgO-Graphite composites (a, b) with a mass ratio of 1:1:0.1. b micrograph is a magnification of the rectangular areas indicated on a figure.

Fig. 5 shows EDS mapping of element C within the composite after different thermal cycles. The flake shaped graphic particles have an orientation perpendicular to the direction of compression in the green pellet (Fig. 5a). After increasing thermal cycles number, graphite flakes start fragmenting into smaller sizes as can be seen in Fig. 5b, c and d. As melting-solidification thermal cycles progressed, the element C is distributed more uniformly due to the particles motion within the composite. The work by Ge et al indicates the existence of a competing mechanism within a composite structure due to different wettabilities of the PCM on the CSM and, that on the carbon material [3, 4]. This competing mechanism leads the formation of microcavities within the composite structure after thermal cycling. Such microcavities provide a route to absorb volume change during phase change. During heating, salt turns into a viscous liquid, providing a capillary force hold the ceramic particle together while avoiding leakage. In the same time, liquid salt moves within microcavities and interparticle pores, generating particle migration and creating a shear force that could break graphite particles. The solidification process could also generate significant stress on the graphite, leading to size reduction. The reciprocating motion of salt causes particle redistribution within the composite, leading to a more homogenous distribution of ingredients.

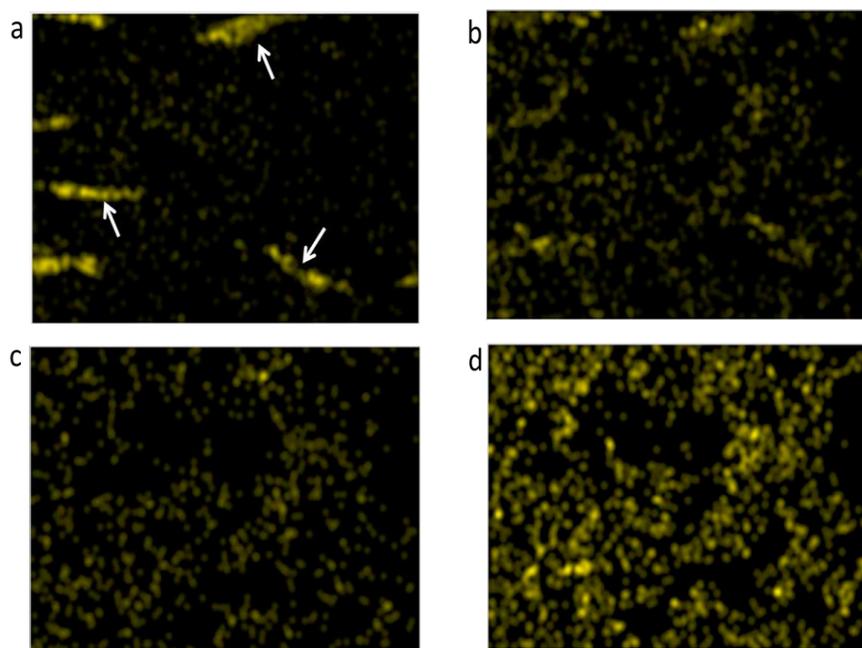


Fig.5. EDS mapping images of C element (yellow colour) within the composite with a mass ratio of 1:1:0.1. (a) Green sample, (b) after 1, (c) 10 and (d) 50 heating and cooling cycles.

5. Conclusions

For the TES technology to be competitive a number of scientific and technologies challenges have to be overcome including TES materials, TES components and devices, and integration of TES devices with energy networks and associated dynamic optimization. This paper focuses on TES materials challenges with a main attention paid to shape stable composite PCMs for medium and high temperature applications. In order to develop TES materials for large scale applications firstly a materials selection methodology has been applied to find the potential candidates for medium high temperature TES. The results of that study shows that molten salts are the most promising candidates. These salts are thermodynamically stable, operate at low pressures and have relatively low costs. However, their applications as PCMs are often hold up by chemical incompatibility and low thermal conductivities. Therefore, an optimization of the formulation of the TES material is the second step of the process. Moreover, also the manufacturing process is taken into account in order to assure a competitive cost of the technology. Thus, cold compression and sintering is an effective way to prepare composite PCMs for industrial

production. Following these methodologies a medium and high temperature TES material has been formulated by a cold compression and sintering method. A eutectic molten salt with a composition of 50 wt.% of Li_2CO_3 and 50 wt.% Na_2CO_3 has been selected as PCM, a ceramic matrix, MgO as a supporting material to prevent the leakage and finally, graphite flakes as the thermal conductivity enhancer. The ratio formulation is 1:1:0.1 respectively. The microstructure of the composite has been studied in order to characterize the stability after different charging/discharging cycles. It has been observed the redistribution within the composite structure of the materials during repeated heating and cooling processes. The solidified molten salt re-returns into viscous liquid when the temperature is above the melting point and flows into the pores and voids due to the volume change. Meanwhile, the viscous liquid phase provides a capillary force to gather and drag the CSM movement with them, which could create stress into the graphite flake structures breaking them after several cycles.

Acknowledgements

This research was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) under grants EP/P004709/1, EP/P003435/1, EP/L019469/1, EP/F060955/1, EP/L014211/1 and EP/K002252/1, the British Council under 2016-RLWK7-10243 and China Scholarship Council (CSC).

References

- [1] M. Aneke, M. Wang, "Energy storage technologies and real life applications-A state of the art review," *Appl. Energy*, vol. 179, pp. 350-377, Oct. 2016.
- [2] Z. Ge, Y. Li, D. Li, Z. Sun, Y. Jin, C. Liu, C. Li, G. Leng, and Y. Ding, "Thermal energy storage: Challenges and the role of particle technology," *Particuology*, vol. 15, pp. 2–8, Aug. 2014.
- [3] Z. Ge, F. Ye, H. Cao, G. Leng, Y. Qin, and Y. Ding, "Carbonate-salt-based composite materials for medium- and high-temperature thermal energy storage," *Particuology*, vol. 15, pp. 77–81, Aug. 2014.
- [4] Z. Ge, F. Ye, Y. Ding, "Composite materials for thermal energy storage: Enhancing performance through microstructures," *ChemSusChem*, vol. 7, no. 5, pp. 1318-1325, 2014.
- [5] C. Y. Zhao and Z. G. Wu, "Heat transfer enhancement of high temperature thermal energy storage using metal foams and expanded graphite," *Sol. Energy Mater. Sol. Cells*, vol. 95, no. 2, pp. 636–643, 2011.
- [6] Bo Zhao, Chuan Li, Yi Jin, Cenyu Yang, Guanghui Leng, Hui Cao, Yongliang Li, Yulong Ding, "Heat transfer performance of thermal energy storage components containing composite phase change materials," *IET Renewable Power Generation*, vol. 10, no. 10, pp. 1515-1522, 2016.
- [7] Chuan Li, Qi Li, Hui Cao, Guanghui Leng, Yongliang Li, Li Wang, Lifang Zheng, Yulong Ding, "Wettability of eutectic NaLiCO_3 salt on magnesium oxide substrates at 778K," *Applied Surface Science*, vol. 442, pp. 148-155, 2018.
- [8] J. Li, L. He, T. Liu, X. Cao, and H. Zhu, "Preparation and characterization of PEG/SiO₂ composites as shape-stabilized phase change materials for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 118, pp. 48–53, 2013.
- [9] S. Karaman, A. Karaipekli, A. Sari, and A. Biçer, "Polyethylene glycol (PEG)/diatomite composite as a novel form-stable phase change material for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 95, no. 7, pp. 1647–1653, 2011.
- [10] W. Wang, X. Yang, Y. Fang, and J. Ding, "Preparation and performance of form-stable polyethylene glycol/silicon dioxide composites as solid-liquid phase change materials," *Appl. Energy*, vol. 86, no. 2, pp. 170–174, 2009.
- [11] N. Vitorino, J. C. C. Abrantes, and J. R. Frade, "Quality criteria for phase change materials selection," *Energy Convers. Manag.*, vol. 124, pp. 598–606, 2016.
- [12] D. Shin and D. Banerjee, "Enhancement of specific heat capacity of high-temperature silica-nanofluids synthesized in alkali chloride salt eutectics for solar thermal-energy storage applications," *Int. J. Heat Mass Transf.*, vol. 54, no. 5, pp. 1064–1070, 2011.
- [13] B. Jo and D. Banerjee, "Enhanced specific heat capacity of molten salt-based nanomaterials: Effects of nanoparticle dispersion and solvent material," *Acta Mater.*, vol. 75, pp. 80–91, 2014.
- [14] G. Qiao, M. Lasfargues, A. Alexiadis, and Y. Ding, "Simulation and experimental study of the specific heat capacity of molten salt based nanofluids," *Appl. Therm. Eng.*, 2016.