

# Microencapsulated phase change materials with high heat capacity and high cyclic durability for high-temperature thermal energy storage and transportation



Takahiro Nomura<sup>a,\*</sup>, Nan Sheng<sup>a</sup>, Chunyu Zhu<sup>a</sup>, Genki Saito<sup>a</sup>, Daiki Hanzaki<sup>a</sup>, Takehito Hiraki<sup>b</sup>, Tomohiro Akiyama<sup>a</sup>

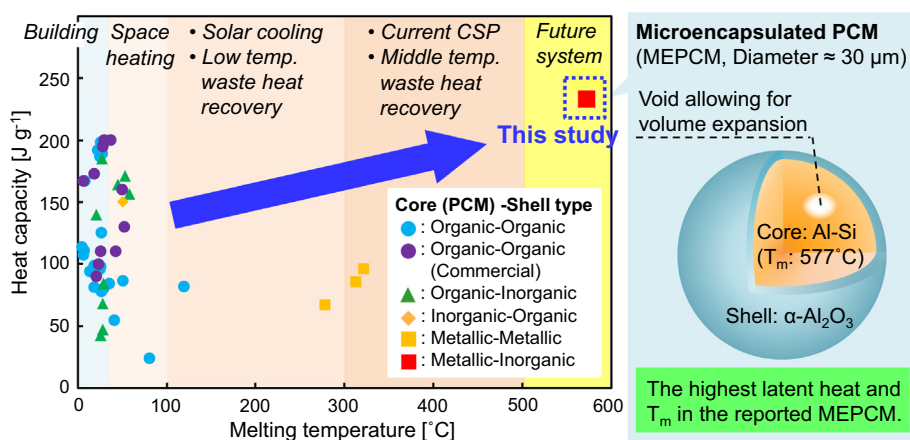
<sup>a</sup> Center for Advanced Research of Energy and Materials, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

<sup>b</sup> Graduate School of Engineering, Tohoku University, Sendai 980-8578, Japan

## HIGHLIGHTS

- Micro-encapsulated phase change material (MEPCM) for high temperature applications are achieved.
- The MEPCM is composed of a stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> shell and Al-25 wt% Si core.
- The MEPCM has an effective void inside the core to allow for volume expansion of the PCMs.
- The MEPCM exhibits excellent durability up to 300 heating and cooling cycles.
- The heat capacity of the MEPCM is five times higher than that of conventional solid sensible heat storage materials.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Latent heat storage (LHS) technology employing phase change materials (PCMs) has received great attention as an alternative to conventional solid sensible heat storage (SHS) for future high-temperature energy utilization systems. In this study, we report the synthesis of a core-shell type microencapsulated PCM (MEPCM) consisting of Al-25 wt% Si microspheres (mean diameter of 36.3 μm and melting temperature of 577 °C) as the core (PCM) and Al<sub>2</sub>O<sub>3</sub> as the shell. The MEPCM was prepared in two steps involving (1) the formation of an AlOOH precursor shell on the PCM microspheres by a hydroxide precipitation process in hot water and (2) heat-oxidation treatment in an O<sub>2</sub> atmosphere to form a stable Al<sub>2</sub>O<sub>3</sub> shell. In particular, the effects of heat-oxidation temperature on the shell morphology, shell crystal structure, mechanical strength, heat capacity, and cyclic durability of the prepared MEPCMs were examined. The resultant MEPCM is composed of a stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> shell and Al-25 wt% Si core with an effective void inside the core to allow for volume expansion of the PCMs during solid-liquid phase transitions. The heat capacity measured for this material is five times higher than that of conventional solid SHS materials. Additionally, the MEPCM exhibits excellent durability up to 300 heating and cooling cycles under oxygen atmosphere. Consequently, it can potentially be used in the next-generation LHS-based high-temperature thermal energy storage and transportation systems.

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\* Corresponding author.

E-mail address: [nms-tropy@eng.hokudai.ac.jp](mailto:nms-tropy@eng.hokudai.ac.jp) (T. Nomura).

## 1. Introduction

Thermal energy storage technology plays a vital role in the high efficiency utilisation of energy since it can provide a buffer against the temporal and spatial mismatches between the energy supply and demand processes. High-temperature sensible heat storage (SHS) using solid materials such as rocks, metals, concrete, sand, bricks, and oxide ceramics [1,2] is one of the fundamental heat utilisation technologies available for the current industrial processes. In order to further advance the SHS technology, tailored structures of the solid SHS materials such as grains, balls, checker bricks, and honeycombs have been fabricated to maximise heat transfer [2]. However, innovative materials with high heat storage capacity have not been synthesised.

A key question is whether conventional solid SHS could serve as the primary storage method for future energy technology. In the field of renewable energy utilisation, the concentrated solar power (CSP) technology is expected to fulfil the base-load and balancing power requirements in the future [3]. Recent innovations in CSP receivers, from trough to central receiver towers, have facilitated an increase in the concentrated temperature and power generation efficiency. As a result, the development of integrated high-temperature thermal energy storage systems with working temperatures up to 1000 °C has become a key requirement for the cost-effective generation of electricity and enhancement of dispatchability [4]. However, the heat storage density of SHS materials is too low for utilisation in future CSP plants, which are expected to generate high outputs and allow 24 h generation. In the area of energy savings, to minimise exergy loss and fuel consumption during chemical production processes and power generation, innovative energy utilisation methodologies such as co-production [5–7], chemical looping [8–11], and advanced integrated coal gasification fuel cell combined cycle (A-IGFC) [12–15] have been proposed. These innovative systems are based on the exergy recuperation concept wherein the exhaust heat from the exothermic process is recycled to the endothermic process. For example, using A-IGFC, generation efficiencies as high as 70–76% can be achieved with enhanced heating values by recycling the exhaust heat from the fuel cells used for coal steam gasification [13]. However, sufficient transfer and recycling of the process heat using conventional solid SHS materials continues to be difficult and challenging owing to insufficient heat capacity.

In this context, latent heat storage (LHS) has received considerable attention as an alternative to SHS for high temperature thermal energy storage. LHS is based on the storage or release of latent heat when a phase change material (PCM) undergoes a solid-liquid phase transition. LHS has the following three advantages over SHS. Firstly, the storage of thermal energy as latent heat yields remarkably high heat storage capacity compared to SHS. Secondly, the PCM can be a constant heat source at the phase change temperature during phase transitions, and thirdly, the reversible phase change process allows for repeated use of the PCM material [16]. Molten salts such as chlorides [17,18], sulfates [19], fluorides [20,21], and carbonates [22], which have melting temperatures,  $T_m$  over 500 °C, have been considered as PCM candidates for high temperature applications. However, it has been pointed out that the thermal conductivity of molten salt PCMs is too low (Ex.  $\text{NaNO}_3$ :  $0.56 \text{ W m}^{-1} \text{ K}^{-1}$ ) to exchange heat rapidly and efficiently. Further, the low thermal stability and high corrosive characteristic of the molten salts have limited their practical use. Therefore, recently, metals and alloys such as Al [23], Al-Si [24,25], Al-Mg-Zn [26], and Cu [27,28] have received significant attention as new high-temperature PCMs, owing to their higher heat capacities, significantly higher thermal conductivities, higher

thermal stability, and lower corrosive feature compared to the conventional molten salt PCMs.

For future high-temperature thermal energy storage, the presently used SHS materials need to be replaced with PCMs, which exhibit much higher heat capacity. At the same time, the basic SHS systems, which are mature technologies and have been optimised from the point of view of effective heat exchange, should be retained. For this purpose, the development of micro-encapsulated PCMs (MEPCMs), the shells of which are composed of ceramics, plays a vital role. The encapsulation of PCMs with ceramic shells can prevent the leakage of liquid PCM during the solid-liquid phase transformation, permitting the use of the encapsulated PCMs as “solids” just like ceramic micro-particles. This means that all the basic SHS technologies with various structures such as grains, balls, checker bricks, and honeycombs can be retained in the new LHS systems by only substituting the SHS materials with the MEPCMs. Fig. 1 shows the conceptual illustration of the next-generation LHS based high-temperature thermal energy storage technology using MEPCMs as the raw materials. In conclusion, MEPCMs covered with ceramic shells can combine the advantages of LHS and SHS, and could potentially advance the next-generation LHS based high-temperature thermal energy storage technology as well as remarkably enhance the SHS technology.

However, the micro-encapsulation of high-temperature PCMs is technically difficult and has not been achieved. Fig. 2 shows the relationship between  $T_m$  and latent heat of the reported nano-/micro-encapsulated with diameters <50  $\mu\text{m}$ , together with their typical applications in each temperature range. Details of the properties and preparation methods of these nano-/micro-encapsulated PCMs are listed in Appendix A. Four core (PCM)-shell type nano-/micro-encapsulated PCMs are reported, including organic-organic [29–48], organic-inorganic [49–55], inorganic-organic [56], and metallic-metallic [57] have been reported. Although core-shell type organic-organic MEPCMs with  $T_m$  under 100 °C are reported, MEPCMs with  $T_m$  over 100 °C have been rarely reported. In particular, there is no report about MEPCMs with  $T_m$  over 500 °C regardless of their necessity. The most serious problem in the micro-encapsulation of high-temperature PCMs with ceramic (inorganic) shells is associated with the development of a capsule structure that can withstand thermal stress associated with volume expansion during the solid to liquid phase transition. Pitie et al. theoretically analysed the mechanical feasibility of coating spherical solid PCM particles with ceramic shells [58]. In that study,  $\text{NaNO}_3$  (the volume expansion ratio because of solid-to-liquid transition was 4.6%) and SiC were assumed to be the PCM and shell material, respectively. It was concluded that PCM capsules which are capable of withstanding the thermal stress arising from the volume expansion accompanying the phase transition of the PCM, can only be realised under limited and highly specific conditions such as using a PCM that exhibits very low volume expansion (close to 0) or with a very thick shell. PCMs with very low volume expansion would have very limited compositions, whereas MEPCMs with very thick shells are likely to exhibit very low heat capacity.

From these discussions, we have realised that it will be a breakthrough technology to prepare a core-shell type MEPCM with a void inside the shell to allow for volume expansion of the PCM during phase transition. To realise this novel concept, we have investigated the preparation of core (= PCM) – shell (= ceramic) type MEPCMs with Al-25 wt% Si microspheres acting as the PCM and the starting material. A facile two-step microencapsulation method is used that involves (1) coating a boehmite ( $\text{AlOOH}$ ) shell on the PCM particles by hydrolysis treatment and (2) heat-oxidation treatment over  $T_m$  of the PCM in an  $\text{O}_2$  atmosphere to transform  $\text{AlOOH}$  to a stable  $\text{Al}_2\text{O}_3$  shell. In our previous study [59], as the

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