Energy 112 (2016) 1074–1083

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

# Radial-like mesoporous silica sphere: A promising new candidate of supporting material for storage of low-, middle-, and high-temperature heat

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ARTICLE INFO

*Article history:*
Received 27 February 2016
Received in revised form
1 July 2016
Accepted 5 July 2016
Available online 5 August 2016

*Keywords:*
Radial-like mesoporous silica
Polyethylene glycol low-temperature phase change material
Lithium nitrate middle-temperature phase change material
Sodium sulfate high-temperature phase change material
Shape-stabilized phase change materials

ABSTRACT

In the study, polyethylene glycol (PEG), lithium nitrate ($LiNO_3$), and sodium sulfate ($Na_2SO_4$) were employed as the low-, middle-, and high-temperature heat storage media, respectively. A series of novel shape-stabilized phase change materials were tailored by a post-preparation method with previously synthesized radial-like mesoporous silica and their structural and thermal properties were characterized. The silica was synthesized through a facile self-assembly process using cetyltriethylammonium bromide as the main template and tetraethyl orthosilicate as silica precursor. The obtained phase change composites showed good shape stability and high thermal energy storage capacity. The morphology and structure of the radial-like mesoporous silica were investigated after combining with different heat storage media. These composites exhibited excellent thermal stability, chemical compatibility, and thermal reliability. The efficient silica support has opened up some new application of energy materials based on novel phase change material/silica composites, such as energy conversion and heat storage for different temperature requirements.

## 1. Introduction

Thermal energy storage technologies have received wide attention because of their critical role in a sustainable energy infrastructure. Thermal energy storage involves the storage of sensible and latent heats. The common latent heat storage materials are phase change materials (PCMs), which can store and release the thermal energy by undergoing phase transition under isothermal conditions [1]. The study on phase change materials was pioneered by Telkes and Raymond in 1940s [2].

PCMs (organic, inorganic, and eutectic) are available for different transition temperatures [3]. Organic phase change materials, such as fatty acids, paraffins, and polyalcohols, together with some inorganic phase change materials, like the hydrated salts, can be applied in a low-temperature environment or at room temperature depending on their melting temperatures. Moreover, molten salts or their mixtures, including chlorides, nitrates, and carbonates, can be applied in the higher temperatures from 120 °C to 1000 °C [4]. Thus, PCMs are further classified into middle- and high-temperature materials, and phase change temperature is the most important property for their desired applications [5].

On the other hand, PCMs can also be divided into four categories: solid–solid PCMs, solid–liquid PCMs, solid–gas PCMs, and liquid–gas PCMs [6] based on their phase change state. Although solid–liquid PCMs had been widely studied, their applications are still limited due to their phase instability in the liquid state. Liquid–solid shape-stabilized PCMs (ss-PCMs) were usually prepared directly by incorporating (molten) PCMs into porous [7]. The ss-PCMs are similar to solid–solid PCMs, which can maintain the solid status even in the phase change process. As a rational alternative to traditional PCMs, ss-PCMs also have the following outstanding features: large energy storage capacity for the phase-transition temperature region, stable shape in the melting state, suitable thermal conductivity, and require no container [8].

For example, Karaman et al. [9] prepared a novel shape-stabilized composite PCM by incorporating polyethylene glycol

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http://dx.doi.org/10.1016/j.energy.2016.07.023

(PEG) into diatomite, and showed that 50 wt% PEG was retained into the pores of diatomite without any seepage. Li et al. [10] prepared several kinds of binary fatty acid/diatomite ss-PCMs by a facile fusion adsorption method, indicating that the latent heat of the composite decreased to 57% of that of capric–lauric acid PCMs and the phase-transition temperature rose slightly from 16.36 to 16.74 °C. Sarı and Karaipekli [11] studied the preparation and thermal properties of palmitic acid (PA)/expanded graphite composite as the ss-PCMs. The carrier successfully retained 80 wt% PCM without leakage from the composite when it was heated above the melting point of PA. The composite sustained 3000 cycles of melting and freezing and hence testified the thermal and chemical reliability of the composite. Investigation by Wang et al. [12] and Luo et al. [13] also demonstrated that PCM shape stabilization was an ideal way to solve the seepage problem of traditional PCMs.

However, it is not difficult for us to perceive that the immersed PCMs are almost focus on low-temperature PCMs. Little information has been carried out on shape-stabilized middle- or high-temperature PCMs, which are used in renewable energy, solar thermal technologies, aerospace applications, steelmaking industry, and efficient utilization of industrial waste heat [5]. Though the study on shape-stabilized PCM started in the 1990s, the preparation method of shape-stabilized PCMs with porous materials was seldom reported, especially for the middle- and high-temperature PCMs. Low-temperature PCMs are always the hot-spot [14]. Investigations, developments and applications in low-temperature PCMs were summarized [15]. However, the applications of PCMs were not limited to the low-temperature environment (about 120 °C).

Porous materials play an important role in energy storage, $H_2$ storage, $CO_2$ sequestration, therapeutics (ex., drug delivery) and catalysis [16]. However, the applications of porous materials in latent heat storage system are still limited. In preliminary studies on organic PCMs using porous support, phase change properties and shape stabilization of PCMs were found to be related to the average pore size of the support [17]. In detail, if the average pore size is too small, the PCM molecular motion will be impeded. This will affect the latent heat storage capacity. On the contrary, if the pores are too large, there will not be sufficient capillary force to stabilize the liquid PCMs. Py et al. [18] once reported that a mesoporous support performs better. Mesoporous silica material has attracted wide attention due to its outstanding properties, such as unique pore structures, large Brunnauere Emmette Teller (BET) specific areas, desirable thermal conductivity, and ecological friendliness [19]. The fibrous structured silica nanospheres have radial-like direct channels and large pore size, which help target molecules to reach the adsorption sites more easily than other mesoporous materials [20].

Studies of silica supporting material in middle- and high-temperature thermal storage system have not been reported. In this paper, polyethylene glycol (PEG), lithium nitrate ($LiNO_3$), and sodium sulfate ($Na_2SO_4$) were selected as low-, middle- and high-temperature PCMs, respectively. Radial-like mesoporous silica (RMS) was synthesized via a facile self-assembly process with cetyltriethylammonium bromide (CTAB) as the main template and Tetraethyl orthosilicate (TEOS) as silica precursor. RMS was employed as the supporting material to prevent the leakage of PCM during the melting process. Thus, three novel PEG/RMS, $LiNO_3$/RMS and $Na_2SO_4$/RMS shape-stabilized composites with enhanced thermal properties for thermal energy storage were prepared via vacuum impregnation and melt-blending method. Then, thermal characterizations of the “phase change RMS” were performed for the preparation of shape-stabilized PCMs.

## 2. Experimental

### 2.1. Materials

The chemicals employed in the study, including Tetraethyl orthosilicate (TEOS, >99%), cetyltriethylammonium bromide (CTAB), ethanol, *n*-pentanol, cyclohexane and urea were purchased from Beijing Chemical Reagent Cp., Ltd. and used as received without any further purification process. Different PCMs including PEG (Mw = 4000), $LiNO_3$ and $Na_2SO_4$ were of analytic grade and purchased from Beijing Chemical Reagent Co., Ltd.

### 2.2. Preparation of RMS support

The RMS support was synthesized from an emulsion system with CTAB as surfactant and TEOS as the source of silica. TEOS was firstly added to 20 mL of cyclohexane containing 1 mL of *n*-pentanol. Then, 20 mL of water containing urea and CTAB was added into this solution and stirred magnetically. Then the mixture was transferred into a Teflon-lined autoclave and heated at 120 °C for 6 h. After cooling to the room temperature, the resultant product was separated centrifugally, washed, and then dried in a vacuum oven at 60 °C for 24 h. After calcination at 550 °C for 2 h, RMS powder was finally obtained.

### 2.3. Preparation of “phase change RMS”

Fig. 1 schematically demonstrates the straightforward preparation procedure of “phase change RMS”. As shown in Fig. 1(a), PEG/RMS ss-PCM was prepared with a vacuum impregnation method [21]. In order to observe the PEG leakage from the composites, the composite PCMs were simultaneously heated at 80 °C during the impregnation process above the melting temperature of the PEG. The resulting PEG/RMS composite was denoted as ss-PCM1. Fig. 1(b) and (c) illustrate the preparation processes of $LiNO_3$/RMS and $Na_2SO_4$/RMS composites with a facile mixing and sintering method, respectively. Firstly, the $LiNO_3$ and RMS powders were mixed in a mixing vessel. Absolute ethanol was then added while stirring. The solution was stirred vigorously at 80 °C, so that the ethanol solvent would evaporate and the $LiNO_3$ and RMS powders were completely mixed. The solution co-blending method was adopted to mix $Na_2SO_4$ powder with RMS powder. The shape stabilization of the $LiNO_3$/RMS composite above $LiNO_3$'s melting point was investigated after sintering at 300 °C for 2 h. The resulting $LiNO_3$/RMS was denoted as ss-PCM2. Similarly, $Na_2SO_4$/RMS ss-PCM was obtained after sintering at 900 °C for 2 h and denoted as ss-PCM3. Only the composite, which has the highest adsorption ratio and maintains its shape without any leakage at the temperature above the melting point of PCM, was recognized as the shape-stabilized PCM. Finally, three kinds of the low-, middle-, and high-temperature “phase change RMS” composites were obtained and denoted as ss-PCM1, ss-PCM2, and ss-PCM3, respectively.

### 2.4. Analysis methods

The specific surface area and pore volume were determined with a $N_2$ adsorption analyzer (Quantachrome Instruments, US). The microstructures of the samples were examined by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, Japan, accelerating voltage 200 KeV). The chemical compatibility of composite PCM was analyzed by the X-ray diffraction (XRD, Model XD-3) and Fourier transform infrared spectroscopy (FT-IR, Model Frontier) method. The XRD patterns were collected at a scanning rate of 4°/min in the $2\theta$ range of 4–80° by using Ni-