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Short communication

# Carbonate-salt-based composite materials for medium- and high-temperature thermal energy storage

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ABSTRACT

This paper discusses composite materials based on inorganic salts for medium- and high-temperature thermal energy storage application. The composites consist of a phase change material (PCM), a ceramic material, and a high thermal conductivity material. The ceramic material forms a microstructural skeleton for encapsulation of the PCM and structural stability of the composites; the high thermal conductivity material enhances the overall thermal conductivity of the composites. Using a eutectic salt of lithium and sodium carbonates as the PCM, magnesium oxide as the ceramic skeleton, and either graphite flakes or carbon nanotubes as the thermal conductivity enhancer, we produced composites with good physical and chemical stability and high thermal conductivity. We found that the wettability of the molten salt on the ceramic and carbon materials significantly affects the microstructure of the composites.

## 1. Introduction

Thermal energy storage plays a vital role in the effective and efficient use of renewable energy resources and industrial waste heat. Keys to thermal storage technology include materials' development and heat exchange during charge and discharge processes. Molten salts are among the most promising phase change materials (PCMs) for thermal energy storage at medium- and high-temperatures. However, applications of molten salts as PCMs are often hampered by chemical incompatibility (such as corrosion of containers) and low thermal conductivities (Guillot et al., 2012; Zhao & Wu, 2011). To overcome these limitations, composites containing carbon allotropes as thermal conductivity enhancing materials (TCEMs) have been proposed. Mixing carbon allotropes with molten salts followed by compression (Acem, Lopez, & Palomo Del Barrio, 2010; Lopez, Acem, & Palomo Del Barrio, 2010) or infiltration of molten salts into a prefabricated carbon (such as graphite foam) (Tammer, 2008) have been shown to be effective approaches for significantly increasing the thermal conductivity of the composites. However, poor dispersion of the carbon in liquid molten salts often leads to the separation of the carbon from the bulk liquid phase of molten salts. Although infiltration of liquid molten salts into prefabricated blocks of carbon materials can avoid this separation issue, the resulting composites are often unable to retain sufficient PCMs within their structures at medium- and high-temperatures, leading to leakage of molten salts during solid–liquid phase change, and hence a decrease in thermal energy storage density of the composites (Pincemin, Olives, Py, & Christ, 2008). Relatively poor wetting between carbon materials and liquid molten salts is an important reason for the leakage and phase separation; the difference in densities of the salts and carbons is also a contributing factor.

In this paper, we introduce microstructured composite materials (intended for medium- and high-temperature applications), consisting of a molten salt-based PCM, a ceramic skeleton as PCM carrier, and a carbon-based thermal conductivity enhancer. We show that the PCM is encapsulated within the composite microstructure, and, the thermal conductivity can be substantially enhanced.

## 2. Experimental

### 2.1. Raw materials and composite fabrication

The PCM used in this work was a eutectic carbonate molten salt ($LiNaCO_3$) made from sodium carbonate ($Na_2CO_3$, Beijing Chemical Works) and lithium carbonate ($Li_2CO_3$, Sinopharm

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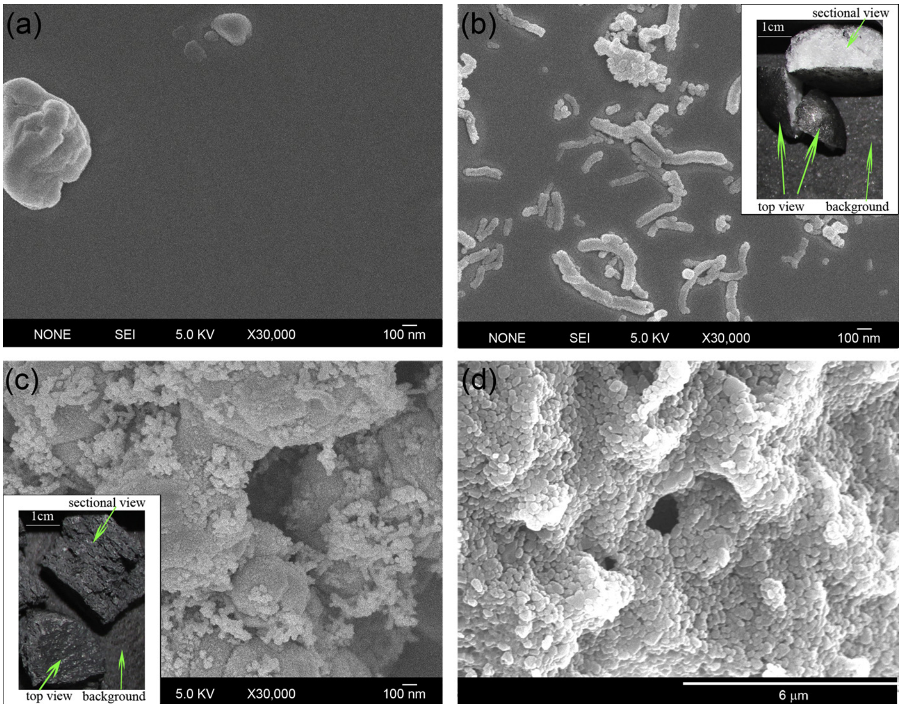

**Fig. 1.** Micrographs of (a) PCM ($LiNaCO_3$), (b) 1PCM/0.01CNTs; inset is a macroscopic optical image. (c) 1PCM/1MgO/0.015CNTs; inset is a macroscopic optical image, and (d) 1PCM/1MgO. Note that in the optical images, the PCM appears white and the CNTs are black.

Chemical Reagent Co. Ltd). Ceramic (MgO, Sinopharm Chemical Reagent Co. Ltd) and carbon materials (natural graphite flakes and carbon nanotubes (CNTs), Beijing Dk Nano Technology Co. Ltd) were chosen as the skeleton material and thermal conductivity enhancer, respectively. The eutectic salt was made by mixing thoroughly 43% $Li_2CO_3$ and 57% $Na_2CO_3$ (mass percentage) and heating the mixture to a temperature above the melting temperature. Fabrication of eutectic based composites involved three steps. First, the eutectic salt was thoroughly mixed with appropriate amounts of ceramic and carbon materials. The mixture was then shaped into disk-like green pellets by uniaxial compression. Finally, the green pellets were sintered in an electric furnace using the following heating procedure: heating from 25 to 400 °C at 5 °C/min, then from 400 to 550 °C at 1 °C/min, and holding at 550 °C for 90 min. The cooling procedure was the reverse of the heating process.

### 2.2. Sample characterization

The morphological and microstructural characterization of the composites was carried out by scanning electron microscopy (SEM, JSM-7100F, JEOL, Japan), and X-ray microtomography (XMT, MicroCT200, Xradia, USA). A Laser flash apparatus (LFA 427, Netzsch, Germany) and a thermal analyzer (TG-DSC, STA 449F3 Jupiter®, Netzsch, Germany) were used to evaluate the thermophysical properties of the samples.

## 3. Results and discussion

### 3.1. Characterization of the composites

Fig. 1 shows SEM images and macroscopic digital photos of some typical samples. The PCM ($LiNaCO_3$) particles exhibit a round shape and a relatively smooth surface (Fig. 1(a)). When CNTs are added, the nanoparticles can only be found at the surface of the PCM particles, as shown in the digital photo in the upper right corner of Fig. 1(b), and almost no CNTs (dark in color) are seen within the bulk of the phase change material (white in color). The cross-sectional and top views of Fig. 1(b) show that the sample is almost semicircular, with CNTs distributed only on the surface of the PCM particles. Fig. 1(c) shows an SEM image of a composite material containing the PCM, MgO, and CNTs in a mass ratio of 1:1:0.015. MgO crystals, with diameters of 0.15–0.6 μm, are distributed uniformly on the surface of the sample. Comparing the insets in Figs. 1(b) and 1(c), we notice that that the CNTs are much better dispersed in the salt in the presence of MgO. Such structural differences between the samples with and without the MgO skeleton material are not only because of the liquid-phase-sintered microstructure (Fig. 1(d)), but are also likely to be associated with interfacial energies between the different components of the composite materials.

Fig. 2 shows XMT images of the samples of different compositons. As shown in Fig. 2(a), the PCM particle after melting and recrystallization has a round shape. Although uniaxial compression was applied during the preparation stage, many pores remain in the PCM structure; these can be attributed to the volume change of the PCM during the melting/recrystallization process. Fig. 2(b) shows the PCM containing CNTs. In this composite, the pores are larger than those in the pure PCM (Fig. 2(a)), and all the CNTs are

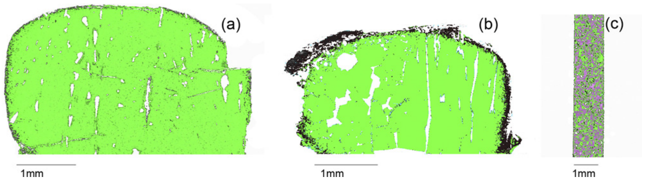

**Fig. 2.** XMT images of (a) PCM ($LiNaCO_3$) at slice 465, (b) 1PCM/0.01CNTs at slice 500, and (c) composite material 1PCM/1MgO/0.015CNTs at slice 531 in the XY planes. Images are obtained from segmentation of the scanned samples by thresholding with Mimics10.0 software; green, black, and pink colors represent PCM, CNTs, and MgO, respectively. (For actual colours mentioned in the text, readers are referred to the on-line web version of this article.)

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