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Gelled graphite/gelatin composites for latent heat cold storage

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HIGHLIGHTS

- The water/graphite suspensions are stabilized with collagen additions.
- Gelation at room temperatures prevents sedimentation of graphite particles.
- The gelled graphite suspensions have enhanced thermal conductivity.
- The thermal response is unchanged upon repeated phase change cycles.

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ABSTRACT

Aqueous suspensions of graphite were shape stabilized by the additions of collagen and characterized as phase change materials for cold storage with enhanced thermal conductivity. Collagen addition stabilized the graphite suspensions in aqueous media without requirements for additional stabilizers or previous functionalization. Gelation at room temperatures prevented sedimentation of graphite particles. SEM of dried samples confirmed nearly random distribution of graphite particles. These gelled suspensions with enhanced thermal conductivity were tested for latent heat cold storage. The thermal response was retained upon repeated phase change cycles, and impedance spectroscopy was used to monitor these cycles. The response time upon phase change was somewhat longer than predicted by taking into account the values of thermal diffusivity and the estimated value of Stefan number, probably due to significant interfacial resistance to heat transfer, combined with discontinuities caused by volume expansion upon phase change.

1. Introduction

Modern societies are urged to develop systems and concepts for efficient and rational use of energy, and to seek increasing use of renewable energies; this requires energy storage to bridge time and/or spatial gaps between availability of renewable energies and consumption, including heat or cold storage, and thermal inertia to minimize energy spent on hot water, heating or air conditioning. The relevant literature thus shows increasing interest on phase change materials (PCMs) for thermal energy storage, based on the high latent heat of melting, often considering hot water applications, using paraffin waxes, fatty acids, etc. However, the low thermal conductivity of these materials is ill suited for fast discharge, thus requiring strategies for faster thermal response [1], including expanded graphite [2,3], carbon nanotubes [4], etc.

The low efficiency of cold production systems also gives opportunities for phase change cold storage [5–7] to enhance performance of air-conditioning heat pumps using ice storage sub coolers [8,9], and more recently phase change slurries for cold storage applications [10–12]. Water stands out due to its abundance, high latent heat density ($\approx$330 MJ m^{-3}), low cost and suitable melting temperature ($\approx$0 °C). The present work was, thus, based on ice/water as a suitable PCM for cold storage. Still, the low thermal conductivity of water, mainly in liquid state, ($\approx$0.6 W m^{-1} K^{-1}), also imposes limitations in discharge rate. A variety of solutions has been tested to improve thermal response of water-based latent heat cold storage, with emphasis on metallic macrostructures (fins, plates, etc.), metallic pieces, and also PCM encapsulation to improve the effective area of transfer [13].

In paraffin/organic based latent heat storage, graphite has been used to improve PCM thermal response due its high thermal conductivity. However, this often requires functionalization in water-based systems or additions of compatibilizers for graphite in water. In addition, the long term applicability is arguable due to insufficient long term stability of graphite suspensions, by sedimentation. Thus, the present work proposes a facile and

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Nomenclature

c_P	heat capacity, J kg^{-1} °C^{-1}
C	capacity, F
d	diameter, m
h	heat transfer coefficient, W m^{-2} K^{-1}
k	thermal conductivity, W m^{-1} K^{-1}
L	length/thickness, m
R	radius
R	resistance, Ω
T	temperature, °C
Z^*	complex impedance, $Z^* = Z' - iZ''$
Z'	real part of complex impedance, Ω
Z''	imaginary part of complex impedance, Ω

Greek symbols

α	thermal diffusivity, m^2 s^{-1}
ρ	density, kg m^{-3}
ϕ	Stefan number, $\phi = c_P \Delta T / \lambda$
λ	latent heat, J kg^{-1}
ω	angular frequency, rad s^{-1}

Subscripts

Al_2O_3	alumina
col	collagen
dis	discharge
exp	experimental
e	external
el	electrode
hf	high frequency
i	internal
lf	low frequency
ref	reference
sample	sample
tc	thermal conduction

inexpensive strategy to prepare water–ice/graphite composites, using collagen as a stabilize agent, to achieve compatibility of graphite in aqueous medium and to prevent sedimentation upon repeated phase change cycles. One expects final costs of <1 € kg^{-1} for production at industrial scale, based on the costs of precursors at industrial scale, i.e., <0.5 € kg^{-1} for graphite [14], and <20 € kg^{-1} for collagen [15].

These composite materials used in cold storage systems can be employed in plates or rods, in which heat charge and discharge occurs by a fluid flow (liquid or gas) across the reservoir surface. The main drawback of the proposed composite materials are related with volume change during solid–liquid and liquid–solid phase changes (≈10%), which can be critical for the reservoir stability. However, the gelled composites allow their use in fragments, promoting a better dimensional adjustment when it comes to the phase change process. With this concept the heat transfer fluid can contact directly the fragments of phase change material improving heat transfer by increasing the contact area between PCM and heat transfer fluid. Dehydration of the composite by the heat transfer fluid should be avoided.

2. Materials and method

Graphite (Merck 1.04206.2500) with particle size below 50 μm and bulk density 280 g cm^{-3} was used to enhance thermal conductivity and collagen (Oxoid LP0008) was used for ready compatibilization of graphite powder in water, and also to prevent sedimentation upon gelation.

Ball milling (*Retsch S1)* was used to reduce the average particle size of graphite particles. Graphite powder was dispersed in collagen solution (5 wt.% relative to water mass) with stirring rate of 20000 rpm during 15 min (*IKA T–25 Ultraturax*). The resulting graphite suspension was then kept under slow stirring, to avoid air incorporation, until gelation.

The homogeneity of graphite distribution was assessed by cryogenic fracture of frozen samples, and by evaluating differences in density between resulting fragments, by the Archimedes method [16]. This method was applied to different graphite contents, up to 30 wt.%. Fragments of selected samples were also dried in air, for up to 1 week and then kept at 100 °C for 1 h, to recover the corresponding porous graphite bodies bonded by dried collagen; this allowed one to perform microstructural characterization by scanning electron microscopy (Hitachi SU1510). Though one also attempted to obtain freeze dried samples, these easily collapsed to loose powders; this may be an indication that graphite/collagen interactions are affected by expansive solidification of water based systems.

FTIR spectroscopy (*Bruker Tensor 27 FT-IR*) was used to characterize absorption bands of collagen and graphite precursors, and corresponding changes upon gelation and after drying, to confirm interactions between graphite and collagen. FTIR spectra for air dried samples (at room temperatures), and freeze dried samples, were obtained to inspect changes in graphite/collagen interactions related to phase change.

DSC (Perkin Elmer (Norwalk, CT) DSC-7, using sapphire as a reference material) measurements were performed on heating from −40 °C to 30 °C, at 5 °C min^{-1} and 10 °C min^{-1}, to evaluate the effect of additions of collagen on the enthalpy of phase change, and to assess if the corresponding temperature is significantly affected, except for the expected effects of heating rate.

Fig. 1 shows the experimental apparatus developed for thermal conductivity measurements, based on steady-state regime, i.e. uniform heat flux from the hot source to cold source, across a series reference/sample/reference association, using reference glass plates with thermal conductivity of 1.18 W m^{-1} K^{-1} and 15 mm thickness. Conservation of heat flux (per unit area) through the sample and reference glass plates yields the following steady-state condition:

$$k_{sample} \frac{\Delta T_{sample}}{L_{sample}} = k_{ref} \frac{\Delta T_{ref}}{L_{ref}} \tag{1}$$

and thus

$$k_{sample} = \frac{k_{ref} \Delta T_{ref} L_{sample}}{\Delta T_{sample} L_{ref}} \tag{2}$$

where k_{ref} represents thermal conductivity of reference glass, L_{sample} the sample length, L_{ref} reference length, ΔT_{ref} the sum of temperature differences across the reference glass plates and ΔT_{sample} the temperature difference across the sample. Temperature was measured with type K thermocouple. Stable temperature in hot/cold sources was controlled by phase change buffers with a suitable difference between melting temperatures at the hot and cold sources. In the actual conditions, the cold source was set by ice/water and the hot source by a phase change material (paraffin wax) with melting temperature of 30 °C. Ready convergence towards steady state results (Fig. 2) demonstrates the reliability of the method. The reliability of the present methods was demonstrated by measurements of standard substances such as water (0.60 W m^{-1} K^{-1}), glycerine (0.30 W m^{-1} K^{-1}) and paraffin wax