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Highly conductive composites made of phase change materials and graphite for thermal storage

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Abstract

Conventional phase change materials (PCMs) are already well known for their high thermal capacity and constant working temperature for thermal storage applications. Nevertheless, their low thermal conductivity (around $1\,W\,m^{-1}\,K^{-1}$) leads to low and decreasing heat storage and discharge powers. Up to now, this major drawback has drastically inhibited their possible applications in industrial or domestic fields. The use of graphite to enhance the thermal conductivity of those materials has been already proposed in the case of paraffin but the corresponding applications are restricted to low-melting temperatures (below 150 °C). For many applications, especially for solar concentrated technologies, this temperature range is too low. In the present paper, new composites made of salts or eutectics and graphite flakes, in a melting temperature range of 200–300 °C are presented in terms of stability, storage capacity and thermal conductivity. The application of those materials to thermal storage is illustrated through simulated results according to different possible designs. The synergy between the storage composite properties and the interfacial area available for heat transfer with the working fluid is presented and discussed.

Keywords: Phase change materials (PCM); Graphite; Latent heat storage; Simulation

1. Introduction

According to the recent increasing constraints, solar thermal electric plants need to be developed in order to decrease the worldwide fuel energy consumption and corresponding CO_2 emission. One of the main limitations of this technology is the variability of the solar energy source. This inhibits the regularity in electricity generation, and thus decreases the overall plant performances and commercial acceptability. In the particular case of concentrated solar technologies, if compared to photovoltaic, the effect of dynamic solar radiation fluctuations induced by passing clouds is also particularly important. Smoothing these natural phenomena by the help of an efficient storage system instead of combination with fossil energy is seen as an attractive solution.

Solar energy is available during the daytime and can be considered in excess during midday hours. The corresponding heat in excess can be collected, stored and subsequently released during the following early morning, the evening and off peak periods. This type of storage is currently named medium term storage.

Three major methods are currently considered for thermal storage: sensible heat, latent heat and thermochemical heat.

In sensible heat storage, thermal energy is stored by changing the temperature of the storage medium, the amount of stored energy depends on its specific heat and on the temperature variation. Mainly dedicated to short-term storage (adapted to treat dynamic variations like cloud effects) using water steam buffer storage, it can also operate for medium-term storage (up to 6 h). As being the simplest technology, it has been well developed and implemented in solar electricity production using thermocline [1] or two tanks systems [2] using molten salt as

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Nomenclature

m	mass (g)
I_{λ}	intensification in thermal conductivity
L	latent heat ($J\,g^{-1}$)
L^{*}	reduced latent heat
L_{g}^{*}	adimensional latent heat
T	temperature (°C)
c_{p}	sensible heat ($J\,g^{-1}\,K^{-1}$)

Greek symbols

λ	thermal conductivity ($W\,m^{-1}\,K^{-1}$)
ρ	density ($kg\,m^{-3}$)

Subscripts

d	decomposition
m	melting
l	liquid
s	solid
max	maximum
i	initial
f	final

storage medium. Nevertheless, molten salts present low thermal conductivities, inducing low charge and discharge power level. Recent research programs like CONTEST [3] and WESPE [4] have led to new material development and test under real "on the sun" working conditions. Ceramic or concrete media were reinforced by stainless steel, improving slightly their thermal conductivity and consequently the obtained power levels. However, the storage capacity was still too low and too large volumes were needed for storage. Moreover, the temperature variations needed for charge and discharge induced structural degradation of the media and difficulties in thermal regulation and control of the whole process [5].

Latent heat storage methods are known to provide higher energy storage densities [6]. Heat is stored by phase change, solid–solid, liquid–solid or gas–liquid of the storage medium. In term of capacity, it also presents the advantage to cumulate the sensible heat corresponding to the temperature difference between charge and discharge steps. Different phase transition for the charge/discharge process can be considered. In practice, solid–liquid phase change is preferred because of simultaneous weak volume variation and important enthalpy variation. It can be principally dedicated to medium term storage but, up to now, no test at industrial scale has been done because of their low thermal conductivity.

The last approach for thermal storage is based on thermochemical reactions [7]. The corresponding performances could allow long-term storage but its technical complexity linked to extensive costs is not easily compatible with cheap solar electricity production.

Within the European programme DISTOR, additional research has been devoted to the development of new storage materials for solar plants based on parabolic trough collectors and direct steam generation technology. The corresponding working temperature is in the range of 490–570 K and the needed thermal conductivity of the storage medium was initially estimated in the range of $8\,W\,m^{-1}\,K^{-1}$.

According to the conclusions of previous studies, the DISTOR project has been based on the latent heat storage approach and more specifically on the solid–liquid transition of phase change materials (PCM). The first step is concerned by the PCM selection based on the following criteria: high storage capacity, low cost, low environmental impact, stability, availability at industrial level and thermal conductivity. Unfortunately, and according to the open literature, most of the PCMs available within the concerned working temperature present thermal conductivities in the range of $1\,W\,m^{-1}\,K^{-1}$ [8,9]. Then, in order to reach the $8\,W\,m^{-1}\,K^{-1}$ target, thermal conductivity enhancement techniques were needed.

Different methods for effective thermal transfer enhancement have been developed: increase in heat transfer area [10], inclusion of conductive fins [11], metal dispersion [12], brushes of oriented or random carbon fibres [13], carbon nanofibres dispersion [14], expanded natural graphite (ENG) impregnation [15]. Among all those methods, only the ENG matrix impregnation led to extensive thermal conductivity intensifications. Compared to the thermal conductivity of the pure tested paraffin ($\lambda = 0.24\,W\,m^{-1}\,K^{-1}$), those of the corresponding composites range up to $70\,W\,m^{-1}\,K^{-1}$ depending upon the ENG amount. Unfortunately, this approach has been only applied to organic PCMs the melting temperature of which is limited to 150 °C. According to current working temperatures of concentrated solar processes, other PCM must be considered, particularly inorganic salts already well known in those applications as heat transfer fluids or sensible heat storage media.

As a matter of fact, numerous PCMs are available in inorganic group [8,9,13–16], but differ extensively in term of practical properties (capacity, corrosion effect, hygroscopic behaviour, price, ...).

In the present paper, new composites made of graphite and inorganic salts adapted to the temperature and power range of concentrated solar applications are presented in terms of elaboration routes and characterisation of storage properties.