



Strongly coupled calcium carbonate/antioxidative graphite nanosheets composites with high cycling stability for thermochemical energy storage

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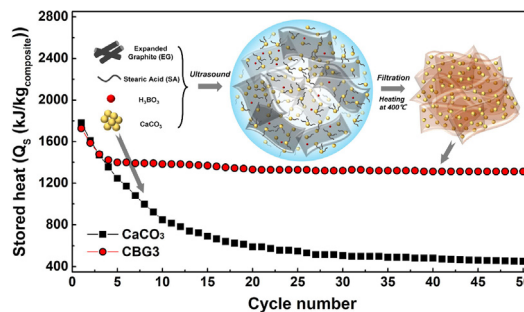
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HIGHLIGHTS

- One-pot route was developed to synthesize CaCO_3 /graphite nanosheets composites.
- H_3BO_3 impregnation enhances the antioxidative ability of graphite nanosheets.
- CaCO_3 /graphite nanosheets composites are highly efficient for heat energy storage.
- The composites show better heat storage performance than pure CaCO_3 .
- Only 3 wt% of graphite nanosheets is required to stabilize the cyclic heat storage.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Concentrated solar power
Thermochemical energy storage
Calcium looping
Graphite nanosheets

ABSTRACT

Reversible carbonation/calcination of CaCO_3 is a promising technology for thermochemical energy storage in concentrated solar power plants. However, the major drawback of this technology is the rapid deactivation of CaO due to sintering. In this study, newly developed CaCO_3 /graphite nanosheets composites were synthesized as the heat storage medium through a one-pot route varying the graphite nanosheets load (3–12 wt%). The impregnation of the composites with H_3BO_3 solutions enhance the initial weightlessness temperature of graphite nanosheets from 900 °C to 1050 °C in pure CO_2 atmosphere, thus upgrading the stability of graphite nanosheets during heat storage/release process. The performances of the synthesized composites were evaluated by thermogravimetric analysis, which simulates the heat storage cycle. The composites showed improved heat storage/output capacity and faster heat input/output rate compared to pure CaCO_3 . Only 3 wt% of graphite nanosheets was needed to effectively stabilize the heat storage capacity of the material. The heat storage capacity of composites with 3 wt% graphite nanosheets is 1313 $\text{kJ/kg}_{\text{composite}}$ after 50 cycles, corresponding to 2.9 times as much as that of pure CaCO_3 . This high stability is attributed to the unique synthetic strategy in which the CaCO_3 nanoparticles uniformly coated on graphite nanosheets surface, and their sintering and aggregation were prevented. This work brings the development of this technology to a level closer to its industrial application.

1. Introduction

In the 21th Conference of Parties (COP21), 195 countries reach a consensus that limiting the increase of global temperature below 2.0 °C

by 2100 [1]. To achieve such an ambitious goal, power produced from renewable energy, especially solar energy, must be massively incorporated into the grid. However, solar energy is characterized by its non-continuous provision of energy, which would affect the operation

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<https://doi.org/10.1016/j.apenergy.2018.09.142>

Received 23 May 2018; Received in revised form 25 August 2018; Accepted 13 September 2018

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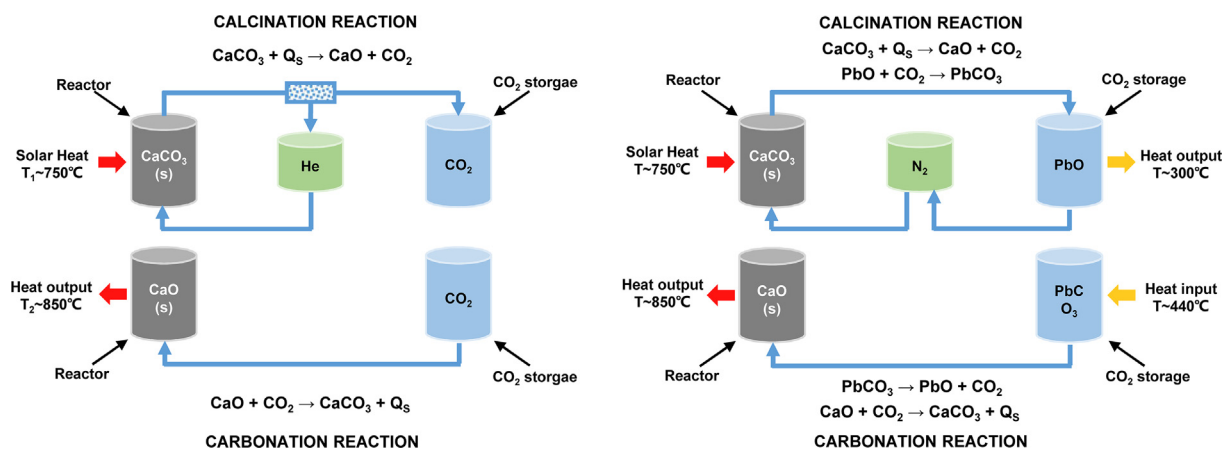


Fig. 1. Schematic diagram of CaO/CaCO₃ chemical heat pump systems.

of the existing energy network [2]. Concentrated solar power (CSP) plants coupling energy storage offers the possibility of storing heat as a primary form of energy for the generation of electricity on demand, thus overcoming the intermittent nature of solar energy [3].

In CSP plants, using reversible gas-solid reactions to store energy has become the focus of current studies [3–5]. An ideal reaction for heat storage need possess high conversion and cycling stability, high enthalpy of reaction and sufficiently fast kinetics. Furthermore, the involved materials should be non-toxic, cheap and abundantly available [5]. Finally, a high temperature of the heat release reaction is necessary to enable high efficiency of the Brayton or Rankine Cycle. Consider the above mentioned requirements, the reversible carbonation/calcination of CaCO₃ ($\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$, $\Delta H_r^0 = -178$ kJ/mol) show great potential due to its high energy density attainable from the reaction enthalpy (~ 1780 kJ/kg_{CaCO₃}) [6] and the wide availability, low cost and nontoxicity of CaCO₃.

The CaO/CaCO₃ heat storage system for CSP plants has been proposed to obtain thermal energy with a higher temperature than that of the original solar thermal energy [5,7,8]. The system consists of heat storage/heat release reactors and CO₂ separation/storage unit (Fig. 1). In the storage mode, the CaCO₃ reactor receives solar thermal energy with a temperature of T₁ (~ 750 °C). Subsequently, CaCO₃ decarbonized to CaO and CO₂ under diluent gas (N₂ or He). There are two approaches for the separation and storage of CO₂: (1) separate the CO₂ in the gas mixture using selective membranes, then store it in compression tanks; (2) absorb the CO₂ by PbO and store it as PbCO₃. In the heat supply mode, pure CO₂ is formed through the decompression of compression tanks or the decarbonation of PbCO₃, and then is introduced into the carbonator. The carbonation of pure CO₂ and CaO generates heat in the carbonator with a temperature of T₂ (~ 850 °C), which is higher than T₁.

Carbonation/calcination looping of CaO has been investigated in the context of CO₂ capture out of flue gas streams for several years (carbonation at ~ 650 °C in $\sim 15\%$ CO₂ and calcination at ~ 900 °C in 100% CO₂) [9–11]. It is observed that the activity of the regenerated CaO rapidly decrease with carbonation/calcination cycle due to the thermal sintering of CaO grains [12–14] and the blocking of the inner pores of CaO particles by CaCO₃ product [15]. A great number of methods have been proposed for enhancing the cycle stability of CaO, including acids pretreatment [16,17], thermal pretreatment [18,19], hydration treatment [20,21] and adding the inert supports, such as Al₂O₃ [22], ZrO₂ [23], CeO₂ [24], MgO [25,26], SiO₂ [27,28], TiO₂ [29], CuO [30] and MnO₂ [31], in the structure of CaO. In recent years, some of these methods were utilized to enhance the heat storage capacity of calcium-based materials under heat storage conditions (carbonation at ~ 850 °C in $\sim 100\%$ CO₂ and calcination at ~ 750 °C in 100% N₂ or He). Valverde et al. [32] explored the effect of thermal

pretreatment on the multicycle activity of limestone-derived CaO. These authors found that the sorbent thermal pretreatment under CO₂ at 960 °C presented a notable reactivation on cycles, an effective conversion of 49% for CaO was reached in the 20th cycle. Benitez-Guerrero et al. [33] investigated the multicycle performance of different Al-composites prepared by milling mixtures of nano-Al₂O₃ and natural limestone powders. The composite with 5 wt% Al₂O₃ presented an effective conversion of 51% after 20 cycles, which is 1.55 times larger than that of raw limestone. Benitez-Guerrero et al. [34] also synthesized CaO/SiO₂ composites by means of a biotemplate method using rice husk as support. The results indicated that the material synthesized with 70 wt% CaO load showed the highest effective conversion, $\sim 34\%$, in the 20th cycle. Obermeier et al. [35] synthesized different Al-composites from Ca-citrate and Al-nitrate, and analyzed their multicycle performance under heat storage conditions. The results indicated that the best material exhibited a molar Ca/Al ratio of 95/5 and the CO₂ uptake capacity after the 20th cycle was 11.8 mmol CO₂/g composite (theoretical value: 17.8 mmol CO₂/g CaO).

Although significant progress has been made, there is still plenty of room to improve the cycling stability of CaO/CaCO₃ heat storage system. The key is to find a more suitable carrier to improve the cyclic stability of CaCO₃. Expanded graphite (EG), possessing high thermal conductivity [36,37] and relatively low density [38], has attracted increasing attention in the production of composites for heat storage [39–41]. Korhammer et al. [42] investigated the hydration/dehydration of CaCl₂ for low-temperature heat storage. They found that the impregnation of CaCl₂ into EG increases the cycle stability, thermal conductivity and the water sorption performance. Mastrorardo et al. [43] developed Mg(OH)₂/EG composites for mid-temperature heat storage. The presence of EG inhibits MgO sintering during hydration/dehydration cycle, thus enhancing the cycle stability. However, although EG have been widely used as the carrier in low-temperature heat storage and med-temperature heat storage, its utilization in high-temperature heat storage, such as CaO/CaCO₃ heat storage system, has not been developed and studied so far. The biggest challenge for the utilization of EG as support in CaO/CaCO₃ heat storage system is that EG is easily oxidized by CO₂ at high temperature (800–900 °C) [44,45].

In this work, the impregnation in H₃BO₃ solution was adopted to enhance the antioxidative ability of EG [46]. Moreover, ultrasonic exfoliation was utilized to dispose EG to form graphite nanosheets (GNSs) [47]. GNSs can be mixed more evenly with CaCO₃ particles than EG, thus can inhibited the sintering of CaCO₃ better. Combining the above two strategies, CaCO₃/GNSs composites were prepared by a facile one-pot process. The structural characteristics, morphology, and heat stability of the novel composites were investigated. Moreover, the heat storage performance of the resulting composites was evaluated through thermogravimetric analysis which simulates the heat storage cycle, and

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