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In-depth investigation of thermochemical performance in a heat battery: Cyclic analysis of K_2CO_3, $MgCl_2$ and Na_2S

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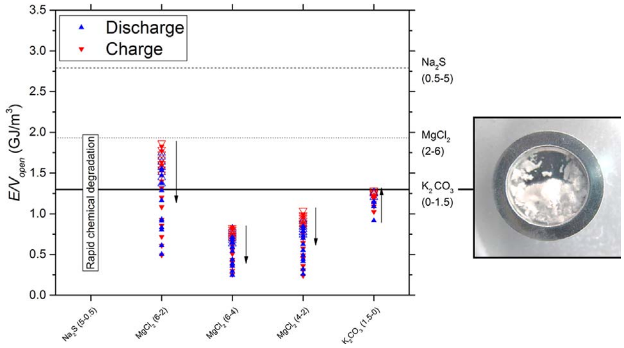
HIGHLIGHTS

- K_2CO_3 is a promising salt for thermochemical heat battery application.
- 1 m^3 of K_2CO_3 can store 15–66 GJ annually, repeated over at least 20 years.
- CO_2 adsorption accompanies hydration of K_2CO_3, without effecting thermochemical performance.
- Na_2S and $MgCl_2$ are salts with a higher storage density than K_2CO_3.
- Na_2S and $MgCl_2$ face chemical degradation in thermochemical heat battery application.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermochemical materials K_2CO_3, $MgCl_2$ and Na_2S have been investigated in depth on energy density, power output and chemical stability in view of domestic heat storage application, presenting a critical assessment of potential chemical side reactions in an open and closed reactor concept. These materials were selected based on a recent review on all possible salt hydrates, within the frame of a thermochemical heat battery and considering recent advances in heat storage application. Judged by gravimetric and calorimetric experiments in operating conditions and worst-case-scenario conditions, K_2CO_3 is recommended for both an open and closed system heat battery. The compound is chemically robust with a material level energy density of 1.28 GJ/m^3 in an open system and 0.95 GJ/m^3 in a closed system, yielding a power output of 283–675 kW/m^3. Na_2S and $MgCl_2$ on the other hand are chemically not robust in heat storage application, although having a higher energy density, output power and temperature in one cycle.

1. Introduction

Society's progressive shift from carbon-based to renewable energy has led to new areas in energy research. The first global conference on energy storage in Paris, 2014 concluded that harvesting, conversion and storage of solar energy is essential to achieve the European goal of an energy-neutral built environment in 2050. The building sector accounts for the largest share of energy consumption (37% Europe wide). As two third of the built environment in 2050 is made up of currently existing buildings, the solution should be realised with the current building stock [1]. Because a significant part (around 70%) of the energy consumption in the European residential sector is related to domestic space heating and hot tap water [2,3] a heat battery technique in view of domestic heat consumption is highly desired.

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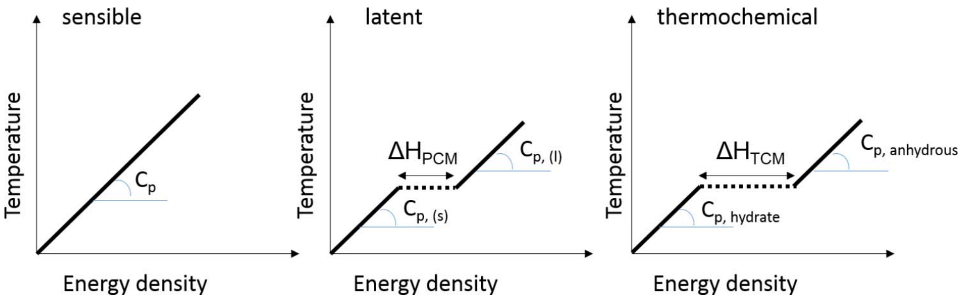

Fig. 1. Schematic diagram of temperature against energy density for sensible, latent and thermochemical heat storage. Sensible heat storage is based on increasing the temperature of a high heat capacity storage material, and hereby storing the heat. Latent heat storage can store a larger amount of heat in a much shorter temperature range, thanks to the phase change. Thermochemical heat storage can store the largest amount of heat, in heatloss-free way by means of chemisorption or physisorption of a sorbent gas.

Given the societal urge for heat storage, the number of reviews on sensible, latent and thermochemical energy storage materials has increased in the past decades, funnelling towards application progressively [4–8].

Heat storage in materials is possible in three ways, shown schematically in Fig. 1. Sensible heat storage is the simplest way to store heat and is based on increasing the temperature of a high heat capacity storage material, hereby storing the heat.

Latent heat storage is based on the released latent heat during a phase transition. A phase change material (PCM) can store a larger amount of heat in a much shorter temperature range [9], thanks to the phase transition:

$$M(s) \rightleftharpoons M(l). \tag{1}$$

A thermochemical reaction on the other hand, can store an even larger amount of heat in heat loss-free way, by means of chemisorption or physisorption of a sorbent gas. As such, high energy density and heat-loss free storage are intrinsic material properties of thermochemical materials (TCM), noticed already in 1958 by Goldstein [10], who was the first to suggest the concept of a thermochemical heat battery. The heat is released when the sorbent gas adsorbs to the storage material [6], reaction (2):

$$M\cdot m\ \ L\,(s) + (n-m)\ \ L(g) \rightleftharpoons M\cdot n\ \ L(s). \tag{2}$$

An essential difference between a phase change and a thermochemical reaction is that a phase change depends on temperature only, whereas a thermochemical reaction has an extra control parameter: namely the pressure of the sorbent (gas), illustrated schematically in the phase diagram in Fig. 2.

In a recent review on advances in thermal energy storage, Lizana et al. [4] conclude that the highest potential for competitive energy efficiency lies in latent and sensible energy storage systems presenting a volumetric thermal energy storage density up to 430 and 250 MJ/m^3 respectively. Application of PCMs in free-cooling ventilation systems and solar energy storage solutions for short and long-term storage periods are highlighted as promising. Their analysis shows that currently, no material for thermochemical energy storage is available that satisfies all the requirements for energy storage solutions for short and long-term storage periods, despite the potentially high energy density achievable (up to 1510 MJ/m^3) and long term storage ability of TCMs. The authors analyse that additional research efforts must be pursued to optimise operation conditions, storage cycle efficiency, material cost and system design.

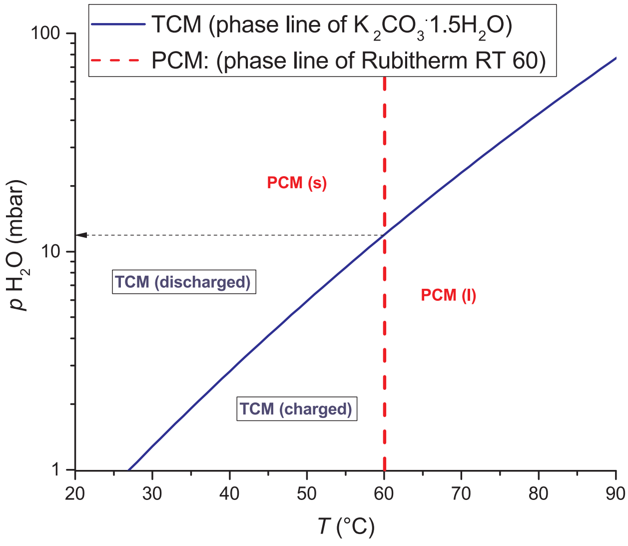

Fig. 2. Schematic phase diagrams of a PCM (K_2CO_3) [11] and a TCM (Rubitherm RT60) [12]. The PCM has a phase transition at 60 °C, regardless of external vapour pressure. The TCM has a phase change at 60 °C when the external vapour pressure is 12 mbar.

Contemporary with Lizana, Donkers [5] had published a review on thermochemical materials, considering operating conditions, volume change, availability, cost and environmental impact in methodological way based on thermodynamic data of 563 thermochemical reactions in total in search for the most promising thermochemical material in view of a technology break-through. Donkers et al. suggested K_2CO_3 for use in domestic application with a volumetric storage density of 1300 MJ/m^3. In line with the review of Lizana, Donkers categorised $MgSO_4$ and $CaCl_2$ unsuitable for low temperature domestic heat storage judged by temperature lift. Furthermore, Na_2S and $MgCl_2$ were noted as TCMs with a higher energy density than K_2CO_3, supporting choices of present research programs [13,14].

Latent heat storage has promising competitive energy efficiency for passive applications like temperature mitigation [15], it is not suitable for thermal energy storage in the form of a heat battery. The low storage density and the difficulty to control the phase change are current barriers to technology break-through in view of longer term storage. Water-based sensible heat storage on the other hand is certainly uncompetitive on material level, considering the average price of 1.20 €/m^3. However, the main bottleneck of sensible heat storage is heat leakage, making storage periods longer than a day impossible. In addition, key performance indicators for sensible heat storage modules in 2020 indicate 300–900 €/m^3 on reactor level [16], mainly due to high isolation costs for the sensible technique.

In recent heat battery projects like MERITS (2007–2013) and E-HUB (2010–2014) thermochemical materials Na_2S and $MgCl_2$ were used, with an average cost of 180 and 650 €/m^3 respectively on material level [5,13,14]. Although $MgCl_2$ was found promising for domestic space heating and hot tap water purposes, later studies of $MgCl_2$ showed that the compound might be less alluring than initially thought, due to chemical degradation with HCl formation inside the reactor [17]. For Na_2S on the other hand, no calorimetric verification of the effective heat output has been reported so far.

It was not until recently that the high impact of chemical stability was recognised on the level of thermochemical reactor design (open or a closed system), discharge periods (days-months) and energy density, as critical reviews and first reactor trials have started just recently. Recent insights request that heat battery targets should be evaluated given the chemical characteristic of the thermochemical material of use.