



Evaluation of a three-phase sorption cycle for thermal energy storage



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ABSTRACT

In recent years, sorption processes are increasingly gaining attention in the field of TES (thermal energy storage), owing to their advantages of high storage density and no significant heat loss during storage process. In this paper, a novel three-phase sorption cycle is proposed and evaluated for TES, to provide cold storage in summer and heat storage in winter. The uniqueness of the cycle is that it allows the solution to reach its crystallized state or even dehydrated state during the charging stage. Three working pairs, namely LiCl/H₂O, CaCl₂/H₂O and LiBr/H₂O, are considered for the proposed cycle based on their pressure–temperature–phase diagrams. Detailed analysis reveals that presence of the three-phase crystallization process could extensively improve the energy storage performance, as heat storage densities increase by 43%, 79% and 38% for LiCl/H₂O, CaCl₂/H₂O and LiBr/H₂O respectively. Overall, LiCl/H₂O is determined to be the best choice among the three couples, with a cold storage density of 519 kWh/m³ (1242 Wh/kg, charged at 90 °C in summer) and a heat storage density of 618 kWh/m³ (1250 Wh/kg, charged at 75 °C in winter). This theoretical evaluation suggests that the three-phase sorption cycle can be a promising solution for TES.

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1. Introduction

Solar energy is currently being regarded as one of the most promising substitutes for traditional energy resources. The use of solar thermal energy has been widely accepted and encouraged for heating, ventilation and air-conditioning in buildings, especially for cooling in summer and heating in winter. Despite the widespread acceptance in solar thermal systems, the main challenge to its application remains to be its unstable feature, which leads to a mismatch between the supply and demand. For this reason, the most efficient and sustainable use of solar energy will be more dependent on the development of reliable and economically viable thermal storage systems.

Traditional methods for TES (thermal energy storage) employ sensible and latent heat techniques. In recent years, STES (sorption thermal energy storage) systems are increasingly gaining credibility as they become promising options for solar heat storage [1]. Their advantages include relatively high storage capacities and the unique function to preserve energy for longer periods with limited heat loss. An approximated calculation made by Hadorn [2] showed that to store 1850 kWh heat, a volume of 10 m³ is required for a

sorption system, which is considerably smaller as compared to a volume of 34 m³ for sensible heat of water (with a temperature difference of 70 °C). This result points out that sorption processes have great potential to be applied for developing compact TES systems.

The term “sorption” has generally been used to cover the technologies such as absorption, adsorption and solid/gas thermochemical reaction. Refrigeration and heat pump systems based on sorption processes have been studied and applied worldwide for several decades. Recently, more efforts have been directed employing sorption processes to store thermal energy. Mugnier and Goetz [3] carried out a theoretical comparison study on the cold storage potential of a series of absorption and adsorption working pairs. Their study showed that solid/gas processes like the reaction between Na₂S and H₂O had the greatest storage capacities. Stitou et al. [4] constructed a solar powered BaCl₂/NH₃ sorption pilot plant with a cooling capacity of 20 kWh, realizing a cold storage density of 114 Wh/kg material at a charging temperature of only 60–70 °C. Li et al. [5] proposed a dual-mode heat transformer, using a heat recovery process to provide heat at appropriate temperature even when the ambient temperature was low. The main drawbacks of solid/gas sorption systems are poor heat and mass transfer properties compared with absorption systems [6]. Other commonly studied sorption couples for STES include zeolite/H₂O [7–11] and silica gel/H₂O [12–14]. Hauer [9] reported a successful open sorption system with 7000 kg zeolite 13X, which was

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Nomenclature

COP	coefficient of performance
C	specific heat capacity, kJ/(kg °C)
CSD	cold storage density, Wh/kg or kWh/m ³
<i>h</i>	enthalpy change, kJ/kg
HSD	heat storage density, Wh/kg or kWh/m ³
<i>m</i>	mass, kg
<i>P</i>	pressure, kPa
<i>Q</i>	heat, kJ
<i>R</i>	gas universal constant, J/(mol K)
<i>r</i>	mass ratio of metal to metal
<i>s</i>	entropy change, J/(mol K)
STES	sorption thermal energy storage
<i>T</i>	temperature, °C
TES	thermal energy storage
<i>V</i>	volume, m ³
<i>w</i>	mass fraction of salt in solution, %
<i>x</i>	water uptake, kg/kg

Greek symbols

η	heat storage efficiency
Δx	water uptake variation per cycle, kg/kg

Subscripts and superscripts

0	standard condition
amb	ambient
bin	binding force
cha	charging
c1–c5	state point in charging stage
con	condensation
cr	crystallization
d	desorption
d1–d3	state point in discharging stage
dis	discharging
eva	evaporation
lv	from liquid to vapor
m	mass
metal	metal components
mono	monohydrate
r	reaction
salt	anhydrous salt
sen	sensible
sol	solution
v	volume
water	water

installed in a school in Munich and connected to the local district heating network to offset the peak energy demands. This large-scale sorption storage system could achieve a heat storage density of 124 kWh/m³. Generally, zeolite is more hydrophilic than silica gel, so desorption temperatures of above 150 °C or even higher than 200 °C are required. This requirement is a major drawback for zeolite/H₂O as compared to silica gel. Jaehnig et al. [13] developed several generations of prototypes in a series of studies and experimentally obtained a heat storage density of 50 kWh/m³, a value less than that obtained through sensible storage of water. Using silica gel/H₂O in closed sorption thermal storage systems is not sufficiently competitive for short-term applications due to its low storage density.

A solar powered LiBr/H₂O absorption refrigeration system with an energy storage function proposed by Xu et al. [15] could theoretically achieve a storage density of 102 kWh/m³. Weber and Dorer [16] developed a NaOH/H₂O absorption prototype for long-term heat storage based on a double stage cycle. For TES systems, higher water uptake variance always leads to better storage performance, however, crystallization of salt solution hinders absorption cycle from reaching a higher salt concentration. Therefore, new designs are needed. Liu et al. [17] and N'Tsoukpoe et al. [18,19] proposed a long-term absorption TES cycle for house heating, which permitted the solution to reach the crystallization point during the storage stage. It is important to note that in this cycle the charging temperature is still restrained since crystallization is only allowed in the storage tank and not in the generator or the reactor. A Swedish company ClimateWell [20,21] has developed several generations of chemical heat pump with integrated heat and cold storage function, using a distinct technology named “three-phase absorption”. It is reported to be capable of storing energy internally with the crystallization process of LiCl salt. This type of commercial machine has been deployed in some solar cooling projects throughout Europe [22–24], whereas detailed information about the basic principle of the so called three-phase absorption process hasn't been clearly addressed.

In this paper, based on the phase diagrams of three common hygroscopic salts with water, namely LiCl/H₂O, CaCl₂/H₂O, LiBr/

H₂O, we have tried to illustrate the principle of the three-phase crystallization process in theory. The effect of the presence of the crystallization process on energy storage density is clearly demonstrated for the first time. In addition, to further increase the storage density, the crystallized salt could be fully charged to lose some or all of crystal water molecules. This improved cycle is suggested to be named “three-phase sorption cycle”. The thorough transformation from solid salt to liquid solution makes it possible to obtain a remarkably higher storage density than other absorption processes.

2. Process description*2.1. Working modes of sorption thermal system*

The working procedures of an STES system can be generally divided into two stages: charging stage and discharging stage. The charging stage consists of a desorption process in a reactor and a gas–liquid condensation process in a condenser. As shown in Fig. 1, when the high temperature heat, collected by a solar collector, is transferred to the reactor, the vapor (sorbate) which clings to the liquid or solid material (sorbent) starts to escape as the threshold binding force between the sorbate and the sorbent is exceeded. The vapor is then channeled through a duct to a condenser at a lower temperature level, where it turns into its liquid state. The condensation heat is released to the surrounding environment – air source, ground source or water source.

Thermodynamically, STES is described as an “indirect” thermal storage approach as compared to other “direct” sensible heat and latent heat methods [25]. The main reason for this classification is that during the charging process, the binding heat, which breaks down the sorption force, is actually stored in the sorbent, while the major part – condensation heat – is not stored in the storage vessels but rather released to the environment. In addition, some amount of sensible heat has to be brought into the system to heat up the sorbent and other components. In general, the heat required during charging stage Q_{cha} can be represented by the following equation:

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