



A zeolite 13X/magnesium sulfate–water sorption thermal energy storage device for domestic heating

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ABSTRACT

A sorption thermal energy storage (TES) device for domestic heating is presented in this article. The TES device adopts the new design scenario with valve-less adsorber and separate reservoir to eliminate the large-diameter vacuum valve for vapor flow, which decreases the cost, reduces the vapor flow resistance, and improves the system reliability. The device is charged by electric heater, which can add much flexibility to the building energy system as well as contribute to the valley filling and peak shaving from the demand side management. The newly developed composite sorbent of zeolite 13X/MgSO₄/ENG-TSA (expanded natural graphite treated with sulfuric acid) with the salt mass fraction of 15% in the zeolite 13X/MgSO₄ mixture is tested and used in the TES device (denoted as XM15/ENG-TSA). Experimental results show that the TES device with XM15/ENG-TSA has the energy storage density of 120.3 kWh m⁻³ at 250 °C charging temperature and 25–90 °C discharging temperature. The temperature lift is as high as 65–69 °C under the adsorption and evaporating temperatures of 25 °C. The impregnated MgSO₄ dramatically improves the temperature rising rate during the adsorption heat recovery process, but the specific energy storage capacity of XM15/ENG-TSA is similar to that of zeolite 13X/ENG-TSA. The effect of the impregnated MgSO₄ suggests that MgSO₄ can be used for low-temperature TES to relieve the self-hindrance of the hydration reaction.

1. Introduction

In the recent decades, increasing energy consumption and depletion of fossil fuels have motivated the world to shift attention to sustainable development [1]. Pursuing better utilization of energy [2] and steering to renewable energy sources [3] have been the two main practical approaches leading to energy conservation and emission reduction. On the one hand, discrepancies between the demand and supply sides of energy lie in many aspects including time, space, and power. On the other hand, some kinds of renewable energy such as solar energy suffer from the defects of intermittence and instability [4]. Energy storage is one of the solutions to these issues, since it is capable of relieving or eliminating the instability and the time discrepancy between energy supply and demand [5]. Compared with mechanical and electrical energy storage, thermal energy storage (TES) enjoys the merits of low cost, suitability for bulk energy storage, and natural combination with solar systems. TES systems implemented in buildings offer a vast range of opportunities and benefits to reduce emissions [6], and they are crucial components of concentrating solar power plants to allow enough dispatchability as well as adapt the electric power production to

the demand curve [7].

TES can be divided into three categories according to the form how energy is stored, i.e., sensible, latent, and thermochemical (including sorption and chemical reaction) heat storage [6]. Sensible heat storage has the advantages of low cost and simple system structure; however, its energy storage density is low. For the sensible heat storage with water as the medium, the energy storage density is approximately 200 MJ m⁻³ for the temperature difference of 50 °C. Latent heat storage uses phase change material (PCM) as the medium, which can store a larger amount of thermal energy with a narrower range of temperature near the phase change temperature of the material compared to sensible heat storage. The energy storage density of PCM is around 300–500 MJ m⁻³ [8]. Thermochemical heat storage has the highest energy storage density compared to sensible and latent heat storage. Depending on the thermochemical heat storage medium, the energy storage density is as high as 1000–2000 MJ m⁻³. Thermochemical materials can store energy at the ambient temperature without self-discharging and experience a significant temperature lift during discharging, which is a crucial character for long-term and seasonal TES [8].

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Nomenclature

c_p	specific heat capacity at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$]
ESC	specific energy storage capacity [J kg^{-1} , Wh kg^{-1}]
ESD	energy storage density [J m^{-3} , kWh m^{-3}]
m	mass [kg]
$\dot{m}$	mass flow rate [kg s^{-1}]
p	pressure [Pa]
Q	heat [J]
q	heat flow [W]
T	temperature [K, $^{\circ}\text{C}$]
$u(y)$	uncertainty of the quantity y
V	volume [m^3]
W	work (electrical) [J]
x	water uptake, adsorption ratio [g g^{-1}]

Greek letters

$\delta y_{\max}$	maximum error of the quantity y
η	energy efficiency
τ	time [s, h]

Subscripts

A	adsorption/sorption, adsorption heat recovery
a	adsorbent/sorbent
C	condensing, condensation
chg	charging
D	desorption, dehydration
dis	discharging
E	evaporating, evaporation
eh	electric heater
f	fluid
max	maximum
min	minimum
R	reservoir
S	sensible heat recovery
sat	saturation

Superscripts

*	normalized
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Among all the energy-consuming sectors, building is responsible for 35% of the global final energy consumption. In China, 71% of the total final energy demand in the residential sub-sector is due to water and space heating [9]. In the United Kingdom, space and water heating accounts for approximately 80% of the energy consumed in the domestic sector, among which direct gas use delivers 72%, and electricity contributes 22% to the heat used for space heating [10]. TES and electricity-to-heat are regarded as the useful approaches to improve the flexibility of building energy systems [11]. Electrically driven thermal energy storage (ETES) system is the combination of the two approaches, which can convert electricity to heat and store the thermal energy when there is excess (renewable) electricity or during off-peak hours. The stored thermal energy is discharged during peak time or periods lacking in renewable electricity [12]. From the concept of demand side management, ETES systems can shift the load of the end-use electricity consumption. The capabilities of valley filling and peak shaving of ETES systems can improve the pattern and magnitude of the electricity consumption. Furthermore, by replacing heat production from fossil fuels, ETES systems can reduce emissions and significantly increase the useful share of renewable energy sources [13]. In consequence, ETES systems with thermochemical materials are promising to be implemented in buildings, as they can deliver high flexibility by the realization of long-term TES within relatively small system sizes and finally contribute to energy conservation and emission reduction.

Physical adsorption, liquid absorption, and chemical reaction are all grouped into thermochemical heat storage [6]. To fulfill the requirement for space heating and domestic hot water, the discharging temperature of the TES system should be in the range of 21–95 $^{\circ}\text{C}$ [11], and the hot water temperature for the heat user can be regulated depending on the user demand. Shigeishi et al. [14] investigated the energy storage properties of molecular sieves 4A, 5A, 13X, charcoal, activated alumina, and silica gel. They found that zeolite 13X is the best adsorbent among these materials. The EU MODSTORE project [15] built a laboratory-scale silica gel–water TES unit which realizes the temperature lift of 15 $^{\circ}\text{C}$ with the maximum adsorption temperature of 70 $^{\circ}\text{C}$ charged by the heating source at 88 $^{\circ}\text{C}$, and the energy storage density is 50 kWh m^{-3} . Dawoud et al. [16] presented a closed-system zeolite 13X–water TES device charged by hot fluid with the energy efficiency of about 0.43–0.67 and the energy storage density as high as 91.76 kWh m^{-3} . The temperature lift of the device is about 30 $^{\circ}\text{C}$ for the heat storage time of 5 h. Tatsidjoudou et al. [17] studied an open-system zeolite 13X–water solar heat storage system for buildings. The

average temperature lift of 38 $^{\circ}\text{C}$ is achieved with 80 kg zeolite 13X. Schreiber et al. [18] applied a closed-system zeolite 13X–water TES unit to the cogeneration in industrial batch processes. They found that adsorption TES has the potential to reduce the primary energy consumption by up to 25%.

It can be concluded that zeolite 13X is one of the best TES materials for domestic heating, as its maximum adsorption temperature can be higher than 100 $^{\circ}\text{C}$. Zeolite 13X also can provide higher temperature lifts than silica gel. The typical regeneration temperature of zeolite 13X is 200–250 $^{\circ}\text{C}$, which can be easily achieved by an electric heater. Consequently, zeolite 13X is chosen as the host porous matrix for the ETES system in this article. The performance of zeolite 13X can be further improved by producing porous matrix composite materials with appropriate chemicals [4]. An alkali and several salts are selected as the optional chemicals for the zeolite 13X-based composite sorbents. NaOH–water absorption is reported to realize the discharging temperature of 40–70 $^{\circ}\text{C}$ at 150 $^{\circ}\text{C}$ charging temperature with the energy storage density of 250 kWh m^{-3} [19]; however, the high corrosion of NaOH is a potentially severe issue. The theoretical energy storage density of MgCl_2 is about 600 kWh m^{-3} . An open-system MgCl_2 –water TES prototype is reported to have the energy storage density of around 140 kWh m^{-3} discharging at 50–64 $^{\circ}\text{C}$ and charging at 130 $^{\circ}\text{C}$ [20], but high charging temperature over 138 $^{\circ}\text{C}$ will result in the decomposition reaction of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ producing MgOHCl , HCl , and water [21]. The theoretical maximum energy storage density of CaCl_2 –water absorption with 80% solid crystals is 263 kWh m^{-3} [22]. CaCl_2 is found to agglomerate and form a gel-like material during hydration, which impedes further water uptake of the salt [23]. Silica gel has been used as the host matrix of CaCl_2 to mitigate the issue of agglomeration. The silica gel/ CaCl_2 materials are reported to have the energy storage density of 211 kWh m^{-3} [24] and the maximum discharging temperature of 63 $^{\circ}\text{C}$ [25]. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has the theoretical energy storage density of 780 kWh m^{-3} and can be dehydrated by 150 $^{\circ}\text{C}$ heating source. The initial experiment of material characterization suggests that the effective energy density is reduced to 420 kWh m^{-3} under suitable operating conditions [26].

Zeolite 13X/ MgSO_4 is a promising composite TES medium for ETES systems. Hongois et al. [27] suggested 15% mass fraction of MgSO_4 be impregnated in zeolite 13X pellets. The test results of the 200 g zeolite 13X/ MgSO_4 sample demonstrate the temperature lift of 33 $^{\circ}\text{C}$ and the energy storage density of 166 kWh m^{-3} which is 27% higher than that of zeolite 13X. Nonetheless, Mahon et al. [28] reported that MgSO_4

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