



Experimental investigation on a dual-mode thermochemical sorption energy storage system



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ARTICLE INFO

Article history:

Received 24 March 2017

Received in revised form

14 August 2017

Accepted 16 August 2017

Available online 25 August 2017

Keywords:

Thermochemical sorption

Dual-mode

Sorption energy storage

Temperature-lift

Energy density

ABSTRACT

A dual-mode thermochemical sorption energy storage system using working pair of expanded graphite/SrCl₂-NH₃ was proposed for seasonal solar thermal energy storage. The proposed system has two working modes to produce useful heat with an expected temperature during the discharging phase according to the different ambient temperatures, including the direct heating supply and temperature-lift heating supply. Solar thermal energy is transformed into chemical bonds and stored in summer, and the stored energy is released in the form of chemical reaction heat in winter. The direct heating supply mode is adopted at a relatively high ambient temperature in winter. The effective energy storage density is higher than 700 kJ/kg and the corresponding system COP is 0.41 when the heat output temperature and ambient temperature are 35 °C and 15 °C, respectively. The specific heating power increases with the decrease of heat output temperature for a given ambient temperature. The temperature-lift heating supply mode is adopted to upgrade the heat output temperature at a low ambient temperature below 0 °C in winter. It can produce heat with a temperature above 70 °C although the ambient temperature is as low as -15 °C. It is desirable to further improve the system performance using low mass ratio and high global conversion. Experimental results showed the advanced dual-mode thermochemical sorption energy storage technology is feasible and effective for seasonal solar thermal energy storage.

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1. Introduction

Energy storage is a key technology to improve the energy utilization efficiency and enhance the energy security for various renewable energy systems. The most research work has focused on the electric battery for energy storage of electrochemical systems. However, more than 90% of the world's primary energy generation is consumed or wasted in the form of thermal energy. Thermal energy storage (TES) plays a broad and critical role in making energy utilization more sustainable for space heating and cooling, solar energy harvesting, solar thermal power generation, and other applications [1].

Solar energy is always suffering from the problem of instability and intermittence due to the variation of solar insolation according to the weather conditions, location, time and seasons of a year. TES is considered as a paramount technology to adjust the instability

and time-discrepancy between energy supply and energy demand. Therefore, reasonable utilization of solar energy inseparably depends on the development of sustainable and economically feasible TES systems. Under this circumstance, an increasing attention has been drawn to seek the possible and suitable solutions to promote TES technology in recent years [2]. Solar thermal energy storage can be divided into short-term storage and long-term/seasonal storage depending on the storage duration. The objective of the former is to store solar heat in sunny days and use it during cloudy days and/or at night, while the latter is to use excess heat collected in the summer to compensate for the heat supply insufficiency during wintertime. Nowadays, the short-term solar heat storage products such as hot water storage tanks and PCMs are available on the market [3]. Xu et al. [4] summarized the latest studies and related projects available for seasonal/long-term storage of thermal energy, including storage materials, existing plants or projects and future outlook. In comparison with the short-term thermal energy storage, long-term seasonal thermal energy storage (STES) is faced with more challenges, which requires larger heat storage capacity and stricter measures to prevent heat losses in the long storage period.

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| Nomenclatures | | | |
|------------------------------|--|------------------|-----------------------------------|
| TES | thermal energy storage | C_p | specific thermal capacity, J/kgK |
| STES | seasonal thermal energy storage | P | pressure, MPa |
| PCM | phase change material | Δt | interval time, s |
| HTDU | high-temperature discharge unit | n | scanning times |
| LTDU | low-temperature discharge unit | m | mass, kg |
| HTR | high-temperature reactor | \dot{m} | mass flow rate, kg/s |
| LTR | low-temperature reactor | ΔH | phase change enthalpy, kJ/kg |
| HTE | high-temperature evaporator | ΔH_r | chemical reaction enthalpy, kJ/kg |
| LTE | low-temperature evaporator | | |
| EG | expanded graphite | <i>Subscript</i> | |
| SHP | specific heating power, W/kg | h | high |
| COP | coefficient of performance | l | low |
| R | mass ratio | c | composite sorbent |
| X | global conversion | cha | charging |
| CM | overall thermal capacity, kJ/K | discha | discharging |
| TSD | thermal storage density, kJ/kg | in | inlet |
| ETSD | effective thermal storage density, kJ/kg | out | outlet |
| | | s | sensible heat |
| | | re | reactor |
| | | ev | evaporation/evaporator |
| | | cn | condensation/condenser |
| | | ad | adsorption |
| | | de | desorption |
| <i>Dimensional variables</i> | | | |
| T | temperature, °C | | |
| $\Delta T'$ | heat transfer temperature difference, °C | | |
| ΔT | temperature difference, °C | | |
| Q | heat quantity, kJ | | |

In addition, the storage material must be economical, reliable and environmentally friendly.

Long-term solar heat storage can be realized by three methods including sensible heat storage, latent heat storage and thermochemical sorption heat storage. Sensible heat storage is a relatively mature technology that has been implemented and evaluated in many large-scale demonstration plants due to its low-cost and reliability. The storage materials are generally water [5], rock-salt material [6] and ground/soil [7]. However, this method has obvious drawbacks of low energy storage density and unsteady heat output temperature. Moreover, the heat output temperature in the discharging process is often at a low level due to the inevitable heat losses during long-term storage.

Latent heat storage using PCM can realize nearly isothermal heat output and the thermal storage density is higher than the sensible heat storage [8]. However, latent heat storage is seldom used for seasonal storage of solar thermal energy. On the one hand, large heat losses would occur unavoidably during the long-term storage. On the other hand, there exists the risk that the discharging process of PCM would happen ahead of time uncontrollably before needed in winter once its temperature is lower than the phase change temperature due to its large heat loss. Moreover, the PCM generally suffers supercooling and corrosion problem, which would severely affect the phase change process [9]. Recently, Dannemand et al. [10] utilized stable supercooling of sodium acetate trihydrate and made it possible to store thermal energy partly loss free in the long-term energy storage process, but the PCM still suffered the deficiency of low energy density. Thus, it is inappropriate for the long-term solar heat storage in most cases.

Thermochemical sorption energy storage has the advantages of higher energy storage density, stable heat output temperature, combined heat and cold storage, integrated energy storage and energy upgrade [11,12]. Besides these advantages, the most remarkable merit is that the thermal energy can be transformed and stored in the form of chemical bonds, which rarely depends on the value of temperature. Thus, the stored thermal energy would

nearly not decrease during long-term storage period (ignoring the sensible heat of material itself). Solid-gas thermochemical sorption energy storage method has been paid much attention in recent years, especially for long-term solar thermal energy storage [13]. For this energy storage method, sorption material and gas are chosen as a sorption working pair. Hydrates and ammoniates (such as $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 8NH_3$, $MnCl_2 \cdot 6NH_3$, etc.) can be employed in sorption processes for seasonal thermal energy storage [14]. Moreover, in order to improve the capacity of heat and mass transfer of sorbent, some composite sorbents made up of salts and porous materials are developed, such as zeolite/ $CaCl_2$ [15], silica gel/salt [16], expanded graphite (EG)/salt [17], form-stable composite zeolite/ $MgSO_4$ [18], etc. The related research results show that composite sorbent is a promising material for long-term solar thermal energy storage. Currently, studies on thermochemical sorption energy storage are still in the theoretical and laboratory testing stage, mostly on fundamental materials, modelling and system optimization.

Mauran et al. [19] constructed and tested a thermochemical sorption energy storage system using $SrBr_2 \cdot H_2O$ sorption working pair, and it was used to fulfill a heating and cooling storage function based on monovariant solid/gas reaction. The prototype allowed heat storage of 60 kWh/m³ at 70–80 °C with a minimum of heat loss over indefinite duration and heat release of 60 kWh/m³ at 35 °C within the floor heating system of a house in mid-season. Obviously, such a low heat output temperature has limited its potential application. Due to the monovariant characteristic of solid-gas chemical reaction, the lower ambient temperature in winter would cause a lower heat output temperature. Moreover, the prototype would be unavailable due to the fact that the water would be frozen if the ambient temperature is below 0 °C. Michel et al. [20] estimated and optimized the performance of a seasonal solid-gas thermochemical sorption process. Experimental results showed that the energy storage density of salt beds could reach about 430–460 kWh/m³, and the specific power between 1.93 and 2.88 W/kg. However, this optimized solid-gas thermochemical

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