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Experimental investigation on thermochemical heat storage using manganese chloride/ammonia

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ABSTRACT

Thermal energy storage plays a key role in the application of renewable energy and low-grade thermal energy. A laboratory test unit of thermochemical heat storage with manganese chloride ($MnCl_2$) as the reactive salt and ammonia (NH_3) as the working gas was constructed, in which expanded graphite was used to improve the heat and mass transfer performance of composite materials. The experimental campaigns show some promising conclusions on the heat storage performances of such a storage unit. With 3.78 kg of composite materials, the highest thermochemical heat storage density is about 1391 kJ/kg when the charging and discharging temperature is 174 °C and 50 °C, respectively. The corresponding volume density of thermochemical heat storage is 179 kWh/m^3. The maximum of thermochemical heat storage efficiency obtained is 48%. The maximum of instantaneous thermochemical heat output power is more than 50 kW. The maximum for the average thermochemical heat output power reaches to 9.9 kW under the experimental conditions. The application prospects of such a thermochemical heat storage system are presented. The promising results have been gained, but some problems must be envisaged. The improvement measures to overcome these problems are also brought forward in order to make the thermochemical heat storage technology realize a successful application in practical systems.

1. Introduction

With the depletion and exhaustion of fossil fuels and the progressive deterioration of the environment, it is urgent to find a better way to use the energy. Thermal energy is one of the main energy consumption types in our daily life. Meanwhile, there is a great deal of waste heat in many industrial processes. Thermal energy storage is a good form of energy management to mitigate the energy challenge and the worsening of the environment nowadays [1]. It not only makes it possible to reuse the waste heat, but also enables the heat to be upgraded by means of the chemical heat pump [2]. Moreover, it can bridge the gap between the demand and the supply of the thermal energy [3]. Thermochemical heat storage has attracted considerable interest in recent years due to its high thermal energy storage density and the distinct advantage for long-term storage with negligible heat loss [4]. The reaction products are separately stored and therefore can realize the transportation of thermal energy. Thermochemical heat storage is more suitable for high-temperature thermal energy transportation, especially when the thermal demand is situated at a long distance from the supply [5]. The investigation on thermochemical heat storage is still on an initial stage, and just a few of such investigations have been made up till now. Many challenges are confronted with the potential application of the thermochemical heat storage [6]. The metal chlorides or bromides are often selected as the thermochemical heat storage materials and either ammonia or water is used for the reactive gas [7]. In many respects, water is the ideal working gas because of the highest latent heat and being non-toxic [8]. However, the low vapor pressure of the water may present problems. The hydration process can be limited by the mass transfer. This will increase the cycle time and is not conducive to the extraction of thermal energy. Compared to water, there is virtually no limit in this aspect when ammonia is used as the reactive gas. Ammonia is often used as the refrigerant for the sorption refrigeration [9]. Besides, ammonia is also employed as the reductant for NOx removal in the vehicle exhaust emission [10], coal-fired power plant and industrial boilers [11]. A major problem with the chemical reactive salts used in the thermochemical heat storage systems is their poor heat transfer properties [8].

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Nomenclature

COP	coefficient of performance
c_p	specific heat ($J \cdot kg^{-1}\ ^{\circ}C^{-1}$)
m	mass (kg)
n	number of moles (mol)
P	pressure (Pa)
q	power (kW)
q_m	mass flow rate of heat transfer fluid (kg/s)
Q	heat amount (kJ)
t	time (s)
T	temperature (K)
V	volume (m^3)
Greek symbols	
γ	thermal energy storage density (kJ/kg or kWh/m^3)
ε	heat output power (kW)
η	thermal energy storage efficiency
θ	Carnot temperature
ΔH	reaction enthalpy (kJ/mol)
Subscripts	
c	condensation
cha	charging
cya	cycled ammonia
cs	composite sensible heat
de	decomposition process
dis	discharging
e	evaporation
eq	equilibrium
f,rin	inlet heat transfer fluid of chemical reactor
f,rout	outlet heat transfer fluid of chemical reactor
hr	heat recovery
hs	heat storage
hsm	heat storage material
in	input
ini	initial
m	mass
M	M point
ms	metal sensible heat
out	output
re	real
ref	reference
s	source
th	theoretical
V	volume

Meanwhile, the swelling and agglomeration phenomena of reactive salts may occur during the chemical reaction process. Salt swelling makes the heat transfer performance degrade, and serious agglomeration phenomenon of the reactive salts diminishes the mass transfer performance [12]. These reasons restrict the practical application of thermochemical heat storage technology. In order to overcome these disadvantages, many researches have been performed on the composite materials [13–16]. The chemical reactive salts are embedded into the porous additives, which have high thermal conductivity and mass transfer characteristics. Touzain et al. [17] pointed out that the use of graphite can not only enhance the heat transfer, but also avoids the agglomeration of ammine crystallites. Tae Kim et al. [18] employed a mixture of expanded graphite and magnesium hydroxide to enhance the thermal conductivity and reactivity of a magnesium oxide/water chemical heat pump. Shkatulov et al. [19] developed a new composite material using magnesium hydroxide and expanded vermiculite.

Thermochemical heat storage is mainly based on the reversible chemical reaction process: A + Heat ↔ B + C. Similar to other thermal energy storage ways, thermochemical heat storage cycle consists of two main processes: charging and discharging. In recent years, both the heat storage materials and systems used for the thermochemical heat storage have been investigated. Even so, the further research on the system design is still needed to resolve some key problems prior to commercial applications [20]. Sakamoto et al. [21] utilized the exothermic chemical reaction between calcium chloride and ammonia for thermal energy storage and studied the influence of a heat transfer media (titanium) on the heat transfer rate of the solid ammoniated salt ($CaCl_2 \cdot mNH_3$). Zhang et al. [22] applied the strontium bromide/expanded vermiculite composite materials to the low-temperature heat storage and the mass energy storage density of 0.46 kWh/kg and volume energy storage density of 105.36 kWh/m^3 were obtained, respectively. Mauran et al. [23] tested a prototype aimed at 60 kWh or 40 kWh for the heating or cooling function based on strontium bromide hydrates ($SrBr_2 \cdot 6H_2O/SrBr_2 \cdot H_2O$). The average heating or cooling power is about 2.5–4 kW, which is far lower than the expected due to the low heat transfer between composite materials and heat exchanger wall. Zondag et al. [24] designed a lab-scale open thermochemical heat storage system using $MgCl_2$ as the reactive material. This thermochemical heat storage system achieves a thermal energy storage density of 0.5 GJ/m^3 (about 139 kWh/m^3). Sakamoto et al. [25] measured the thermophysical property of ammoniated salt for thermochemical heat storage system using $CaCl_2$–NH_3 as working pair. Pardo et al. [26] investigated a $Ca(OH)_2/CaO$ thermochemical heat storage system in a fluidized bed reactor and obtained the heat storage density of 156 kWh/m^3.

In this work, the manganese chloride ($MnCl_2$) is used as the thermochemical heat storage material and ammonia is used for the reactive gas. The chemical reaction equation between manganese chloride and ammonia is described as:

$$MnCl_2 \cdot 2NH_3 + 4NH_3 \Leftrightarrow MnCl_2 \cdot 6NH_3 + \Delta H \quad (1)$$

The use of expanded graphite to increase the thermal conductivity of thermochemical heat storage materials in the chemical reactor has been proved. Expanded graphite has high thermal conductivity and exhibits good mass transfer characteristics, chemical durability and easily forms the heat exchange structure [18]. Hence, in our study, the expanded graphite is also chosen as the additives to enhance the thermal conductivity of thermochemical heat storage materials, and improve the mass transfer performance of chemical reactive salts as well. This paper focused on the heat storage capacity of the prepared consolidated composite materials in thermochemical heat storage systems. Moreover, we dedicate to addressing the correlations of different parameters under the operating conditions in a lab-scale test unit. Thus, an experimental investigation of a thermochemical heat storage system was performed. It aims at:

- determining the performance of thermochemical heat storage system under the specified operation conditions;
- analyzing the relevance of the operating parameters for the thermochemical heat storage system;