Applied Thermal Engineering 91 (2015) 377–386

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research paper

Energy density enhancement of chemical heat storage material for magnesium oxide/water chemical heat pump

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HIGHLIGHTS

- A new chemical heat storage material, donated as EML, was developed.
- EML composite made from pure $Mg(OH)_2$, expanded graphite and lithium bromide.
- EML tablet was demonstrated by compressing the EML composite.
- Compression force did not degrade the conversion in dehydration and hydration.
- EML tablet demonstrated superior heat storage and output performances.

ARTICLE INFO

Article history:
Received 22 July 2015
Accepted 4 August 2015
Available online 13 August 2015

Keywords:
Thermochemical energy storage
Magnesium hydroxide
Expanded graphite
Lithium bromide
Volumetric heat storage/output performances

ABSTRACT

A novel candidate chemical heat storage material having higher reaction performance and higher thermal conductivity used for magnesium oxide/water chemical heat pump was developed in this study. The material, called EML, was obtained by mixing pure $Mg(OH)_2$ with expanded graphite (EG) and lithium bromide (LiBr), which offer higher thermal conductivity and reactivity, respectively. With the aim to achieve a high energy density, the EML composite was compressed into figure of the EML tablet (ϕ7.1 mm $\times$ thickness 3.5 mm). The compression force did not degrade the reaction conversion, and furthermore it enabled us to achieve best heat storage and output performances. The EML tablet could store heat of 815.4 MJ m_{tab}^{-3} at 300 °C within 120 min, which corresponded to almost 4.4 times higher the heat output of the EML composite, and therefore, the EML tablet is the solution which releases more heat in a shorter time. A relatively larger volumetric gross heat output was also recorded for the EML tablet, which was greater than one attained for the EML composite at certain temperatures. As a consequence, it is expected that the EML tablet could respond more quickly to sudden demand of heat from users. It was concluded that the EML tablet demonstrated superior performances.

1. Introduction

Thermal energy storage is an important part of the overall solution to serious environmental problems; especially global warming and natural resource depletion, and to achieve sustainable development without sacrificing economic growth. Thermal energy storage is a technology which designed to accumulate energy when production exceeds demand and to make it available at the user's request. There are three kinds of thermal energy storage systems, namely: 1) *sensible heat storage* that is based on storing thermal energy by temperature change of liquid or solid storage medium (e.g. water, sand, molten salts, rocks), with water being the cheapest option; 2) *latent heat storage* using phase change materials (e.g. between a solid state and liquid state); and 3) *thermochemical energy storage* using chemical reactions for storing and releasing thermal energy. Among these thermal energy storages, the thermochemical energy storage is considered as the most promising thermal energy storage candidate because of higher energy density

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http://dx.doi.org/10.1016/j.applthermaleng.2015.08.008
1359-4311/

of the occurring reversible chemical reactions, which can be even higher than what is usually encountered for the other thermal storage processes: sensible and latent heat storages [1–3].

At medium temperature range between 300 and 400 °C a magnesium oxide/water (MgO/H_2O) chemical heat pump is one of candidate thermochemical energy storages, and it has been studied in this study. The MgO/H_2O chemical heat pump uses a reversible chemical reaction between MgO and H_2O for thermal energy storage and transfer, and it is based on the following equilibria [4]:

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s) \quad \Delta H_r^\circ = -81.0 \text{ kJ mol}^{-1} \tag{1}$$

$$H_2O(g) \leftrightarrow H_2O(l) \quad \Delta H_s^\circ = -41.0 \text{ kJ mol}^{-1} \tag{2}$$

The forward reaction in Eq. (1), *hydration*, is exothermic and corresponds to the heat output operation of the heat pump system. The backward reaction in Eq. (1), *dehydration*, is endothermic and corresponds to the heat storage operation. Based on $Mg(OH)_2$ dehydration and MgO hydration, respectively, heat can be stored at around 300–350 °C and re-utilized at temperatures between 110 and 150 °C. Even though pure $Mg(OH)_2$ and MgO are considered as promising pure materials for the thermochemical energy storage in terms of its low cost, stability, non-toxicity, the MgO/H_2O chemical heat pump is still difficult to be deployed in a practical application due to two issues involved in properties of pure materials such as heat transfer property and reaction performance.

The limitation of heat transfer is because of the low thermal conductivity of pure $Mg(OH)_2$ and MgO. For instance, a packed bed of manufactured pure $Mg(OH)_2$ pellets (ϕ2 mm × 10 mm of average length) provided a thermal conductivity around 0.15 W m^{-1} K^{-1} [5]. For enhancement of thermal conductivity, expanded graphite (EG) as a high thermal conductive material is a good choice to be mixed with pure $Mg(OH)_2$ powder, which not only increases the thermal conductivity of the pure materials by a factor of 5–10, but also creates a kind of carrier structure that avoids the agglomeration of particles of pure materials [6–9]. Thereby, a mixture of $Mg(OH)_2$/EG has been demonstrated and the thermal conductivity of the $Mg(OH)_2$/EG mixture was measured after forming a slab (20 mm × 45.2 mm × 110 mm). It has been reported that the thermal conductivity of the $Mg(OH)_2$/EG slab with mass ratio of $Mg(OH)_2$:EG = 8:1 resulted in 1.2 W m^{-1} K^{-1}, which was more than 8 times larger than the thermal conductivity of manufactural $Mg(OH)_2$ pellets (0.15 W m^{-1} K^{-1}), and moreover, a continuous tight contact between the storage composite and the wall of the heat exchanger was obtained [10]. Even though first issue involved in the heat transfer properties could be solved by introducing of EG, reaction performance of pure materials for relevant to another issue for MgO/H_2O chemical heat pump is remained; since EG is a carbon based material.

Several investigations have been reported regarding the improvement of reaction performance of pure material for the MgO/H_2O chemical heat pump [11–13], because it is essential that the heat storage material be developed. From these studies, it has been well established that the reaction performance, and in particular the dehydration and hydration reactivities could be enhanced by surface modification via high hygroscopic compounds such as LiCl, NaCl, LiOH, NaOH [11–13]. These hygroscopic compounds act to accelerate the release of the H_2O product during dehydration and to attract H_2O from the surroundings during hydration, thus increasing the reactivity. The hygroscopic property is determined by the value of enthalpy changes during dissolution into water (ΔH_{sol}) and thereby, in case a compound having a large negative value of ΔH_{sol} can be a candidate for reactivity enhancer. For candidate hygroscopic compounds such as LiCl, NaCl, LiOH, NaOH an order of ΔH_{sol} values is NaOH (−44.52 kJ mol^{-1}) < LiCl (−37.03 kJ mol^{-1}) < LiOH (−23.56 kJ mol^{-1}) < NaCl (3.88 kJ mol^{-1}). Even though metal hydroxides have large negative values of ΔH_{sol}, they are not suggested to use as the reactivity enhancer due to their strong basic property [13]. Ishitobi et al. [13,14] developed new chemical heat storage material, which was proposed to use for MgO/H_2O chemical heat pump, by mixing LiCl to pure $Mg(OH)_2$; since LiCl showed large negative value of ΔH_{sol} so far. The mixture of LiCl/$Mg(OH)_2$ demonstrated the higher reactivity due to high hygroscopic property of LiCl and moreover, LiCl/$Mg(OH)_2$ had a high heat output density. However, the limitation of heat transfer was still remained for the mixture of LiCl/$Mg(OH)_2$.

With the aim to achieve a high reaction performance and high thermal conductivity at same time, a novel candidate chemical heat storage material, named EML, was developed. It was obtained by mixing pure $Mg(OH)_2$ with EG and lithium bromide (LiBr), which offer higher thermal conductivity and reactivity, respectively. A potential of the EML composite, and the effects of LiBr and EG on dehydration and hydration reactivity were kinetically investigated based on thermogravimetic analysis in our former studies [15–18]. It was experimentally demonstrated that LiBr was successfully employed as reactivity enhancer because of its strong hygroscopic property which proven by its ΔH_{sol} value of −48.80 kJ mol^{-1}, which was largest negative value among high hygroscopic compounds reported, and particularly, it was negatively greater than that recorded for LiCl (−37.03 kJ mol^{-1}). The contribution of LiBr into the EML composite also results in good adhesion between $Mg(OH)_2$ particles and the EG surface. For further studies of determining the optimal mixing ratios of LiBr and EG in the EML composite, the experiments were carried out at five different mixing molar ratios of LiBr-to-$Mg(OH)_2$, α: 0.300, 0.100, 0.050, 0.010, 0.005, and seven different mixing mass ratios of EG-to-$Mg(OH)_2$, w: 0.50, 0.67, 0.75, 0.80, 0.83, 0.86 and 0.88 from which the kinetic parameters, i.e., the reaction rate constants and activation energies, were obtained for both reactions. The investigation revealed α of 0.10 ($Mg(OH)_2$:LiBr = 10:1) and w of 0.83 ($Mg(OH)_2$:EG = 5:1) were the optimal mixing molar and mass ratios based on the evaluation of kinetic parameters [17,18].

The objective of this study is to achieve higher energy density for the chemical heat storage material used for MgO/H_2O chemical heat pump, and thereby, the EML tablet (ϕ7.1 mm × thickness 3.5 mm) was demonstrated by compressing the EML composite with optimal mixing ratios of α = 0.10 and w = 0.83. Dehydration and hydration behavior of the EML tablet (α = 0.10 and w = 0.83) was investigated experimentally based on thermogravimetric method, and strength points for tablet formation were discussed comparing with the results of the composite. The thermal conductivity measurement was carried out by a quick thermal conductivity meter in order to quantify the enhancement in thermal conductivity, which achieved via presence of EG in the EML. Then, tablet volumetric heat storage and output performances of the EML tablet were evaluated based on the results of dehydration and hydration, respectively.

2. Experimental section

2.1. Sample preparation

Firstly, the EML composite was prepared by comprising pure $Mg(OH)_2$ powder (0.07 μm and 99.9%), lithium bromide monohydrate ($LiBr \cdot H_2O$, 99.5%), which provided by Wako Pure Chemical Industries, Ltd., and EG. For preparation of EG, raw-expandable graphite (SS-3, Air Water Inc.) was heated at 700 °C for 10 min in an electric muffle furnace. A simple and high-yield impregnation method was used to prepare the EML composite as follows: