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The optimization of mixing ratio of expanded graphite mixed chemical heat storage material for magnesium oxide/water chemical heat pump

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HIGHLIGHTS

- The expanded graphite (EG) mixture was developed for MgO/H_2O chemical heat pump.
- Optimization of mixing molar ratio between $Mg(OH)_2$ and $CaCl_2$ was conducted.
- The hydration reactivity of mixture was decreased as the mixing molar ratio increased.
- Heat output rate and capacity of optimized EG mixture was estimated.
- Optimized EG mixture shows better heat output performance than pure $Mg(OH)_2$.

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ABSTRACT

A chemical heat storage composite material (EMC), a mixture of expanded graphite (EG), magnesium hydroxide ($Mg(OH)_2$), and calcium chloride ($CaCl_2$), was developed as a magnesium oxide/water chemical heat pump reactant. The potential of the EMC was confirmed and optimized mixing weight ratio between EG and $Mg(OH)_2$ was suggested in previous study. In this study, the optimization of mixing molar ratio between $Mg(OH)_2$ and $CaCl_2$ for practical application was conducted; total six kinds of EMC mixtures, which have different mixing molar ratio from 0, to 0.01 to 0.20 with optimized mixing weight ratio, were prepared then dehydration and hydration experiments were carried out. From experimental results, it was confirmed that hydration reacted conversion was increased as increasing amount of $CaCl_2$ in an EMC and the optimized mixing molar ratio was suggested as mixing molar ratio, α, is 0.1 at mixing weight ratio, n, is 0.8 by considering chemical rate constant and reacted conversion. Hydration under various vapor pressures and temperatures of optimized EMC was also conducted and optimized EMC showed better performance than pure $Mg(OH)_2$. Finally, the heat output performance of optimized EMC was estimated numerically. In conclusion, optimized EMC performed better on dehydration and hydration than pure $Mg(OH)_2$ by adding EG, which has high thermal conductivity and large specific surface, and $CaCl_2$, which has hydrophilic property.

1. Introduction

Thermal energy storage is considered as an advanced energy technology, and there has been an increasing interest in the use of this essential technique for the thermal applications such as heating, hot water, air conditioning, and so on [1]. Chemical heat pump (CHP) system utilize the reversible chemical reaction to store and change the temperature level of thermal energy by using chemical substance [2]. In particular, a CHP that uses the chemical reaction between water (H_2O) and magnesium oxide (MgO), as shown in Eqs. (1) and (2), has been studied by the authors' group [3,4].

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

$$H_2O(g) \leftrightarrow H_2O(l) \quad \Delta H^\circ = -40.0\ \mathrm{kJ \cdot mol^{-1}} \tag{2}$$

Fig. 1 shows the operation of a MgO/H_2O CHP system that store the thermal energy via the dehydration of magnesium hydroxide ($Mg(OH)_2$), endothermic reaction, as shown in Fig. 1(a), and release the stored energy on demand via the hydration of magnesium oxide, exothermic reaction, in Fig. 1(b). The heat pump would be

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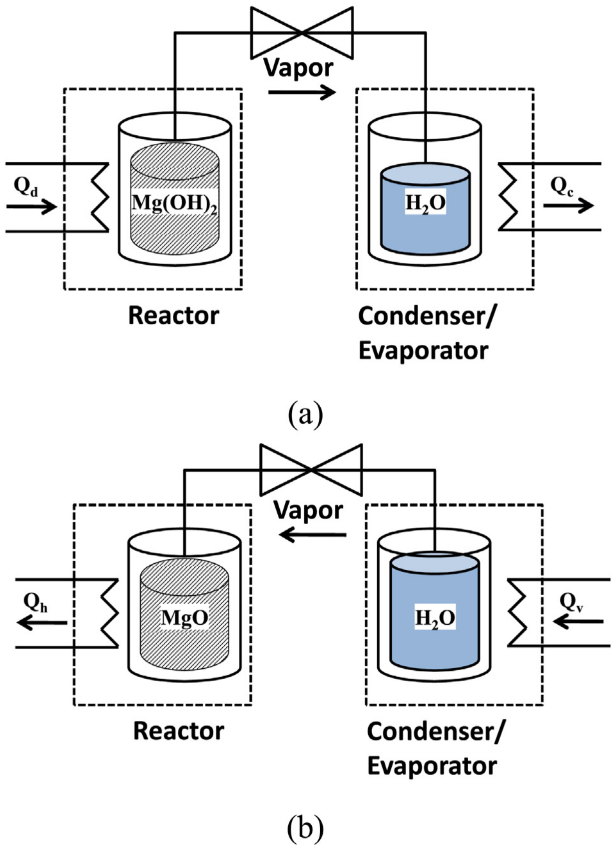

Fig. 1. Principles of the magnesium oxide/water chemical heat pump: (a) heat storage operation and (b) heat supply operation.

unique system that can store heat at around 300–400 °C and release heat at around 100–200 °C with the heat amplification under less than atmospheric pressure. The advantages of the chemical heat pump are that it can store exhaust or surplus heat generated from a cogeneration process, the reactant materials are safe, economical and environmentally friendly, and the heat can be stored for longer periods without heat losses than other conventional heat storage ways [5].

Due to the low thermal conductivity of magnesium oxide, the increasing or decreasing of bed temperature, as endothermic or exothermic reaction process, takes a long time, such as 3 h. This causes a decrease in the driving force for the reaction, since it may be expressed as a difference of pressure at the gas phase and the solid reactant for the equilibrium pressure [6]. Methods for enhancement of the thermal conductivity of reaction materials for a packed bed reactor in a chemical heat pump have been investigated. One promising method is the introduction of carbon based materials that is carbon nanofibers, carbon nanotubes, and expanded graphite into heat storage reactants [7]. In this study, expanded graphite (EG) was selected among the carbon based materials because EG has a high possibility of mass production and cost performance. EG is known as flexible and porous graphite and it was reported that the heat transfer and reactivity of reactants for solid–gas chemical heat pumps was improved by the mixing EG and solid reactants [8]. EG is also durable at high temperatures and chemically inert. EG with special designed properties to satisfy different demands in industrial also has been widely used as a kind of functional carbon material in sealing, catalyzing, mechanical parts for space flight, military affairs, and environmental protection [9,10].

The potential of material mixed with expanded graphite (EG), magnesium hydroxide ($Mg(OH)_2$), and calcium chloride ($CaCl_2$), referred to as EMC, was confirmed [11] and the optimization of mixing weight ratio of EMC between $Mg(OH)_2$ and EG in EM, mixture of EG and $Mg(OH)_2$, for practical application was discussed and optimized mixing weight ratio was suggested in previous studies [12].

As a series of above mentioned studies, optimization of mixing molar ratio of EMC, between $Mg(OH)_2$ and $CaCl_2$ in EMC, was discussed and the optimized mixing molar ratio for practical application was suggested in this study. Furthermore, hydration and heat output performance of optimized EMC was also examined and estimated.

2. Experimental

2.1. Expanded graphite

For production of expandable graphite, it is possible to insert various atomic or molecular layers of a different chemical species, halogens, alkali metals, sulfate, nitrate, and various organic acids, as intercalation between graphite layers in a graphite host material due to the weakness of the van der Waals-type forces [13,14].

In this study, the expandable graphite flake (SS-3, Air Water INC.) was used as graphite intercalation compound [15]. The flake was heated at 700 °C for 10 min in a furnace, and the intercalated reagent decomposed and changed into the gas product and the graphite layers were expanded by gas generation. The resulting expanded graphite material increased in volume of ≥180 mL/g that has over 100 times volume of its original flake [16]. The morphologies of EG were observed by SEM (SM-200, TOPCON Corp.) and it shows that small abundant honeycomb pores by expansion of raw EG flake in Fig. 2(a). The pores are used as a binder to improve heat and mass transfer in the bed, and, the furrows resulting from the parting of graphite layers in EG provide channels for retaining the $Mg(OH)_2$ powder and facilitating the transport of gas phase materials [17].

There are two different ways to use EG to improve the overall thermal properties of materials: the one is blend method and the other is fin method. In this study, blend method, developed in institute des materiaux et procédés (IMP) in Perpignan, France at 1983, based on intimate mixing the EG powder with magnesium hydroxide to insert the magnesium hydroxide particles in the small pores of expanded graphite, was tried [18,19].

2.2. Preparation procedure

First of all, mixing weight ratio, n, and mixing molar ratio, α, of EMC was defined as follow equations, Eqs. (3) and (4).

$$\text{Mixing weight ratio}(n) = \frac{w_{Mg(OH)_2}}{w_{EG} + w_{Mg(OH)_2}} \quad (3)$$

$$\text{Mixing molar ratio}(\alpha) = \frac{\text{mole number of } CaCl_2 \text{ in EMC [mole]}}{\text{mole number of } Mg(OH)_2 \text{ in EMC [mole]}} \quad (4)$$

The synthesized material of expanded graphite, magnesium hydroxide (99.9%, primary particle diameter of 0.07 μm, Wako Pure Chemical Industries, Ltd.), and calcium chloride (99.9%, Wako Pure Chemical Industries, Ltd.) with optimized mixing weight ratio ($n = 0.8$) and six different mixing molar ratios ($\alpha = 0$, 0.01, 0.05, 0.10, 0.15, and 0.20) were prepared by following procedure [20].