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Lithium bromide-mediated reaction performance enhancement of a chemical heat-storage material for magnesium oxide/water chemical heat pumps

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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.
- LiBr was capable of being a reactivity enhancer.
- EML composite could dehydrate and hydrate at the same reaction temperature (200 °C).
- The heat out capacity of the EML composite was larger than that of pure $Mg(OH)_2$.
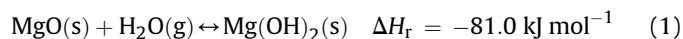
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ABSTRACT

The reaction performance enhancement of a chemical heat-storage material for a magnesium oxide/water chemical heat pump was discussed. A new composite, denoted as EML, was developed by mixing pure magnesium hydroxide with lithium bromide and expanded graphite, which were employed as reactivity and heat transfer enhancers, respectively. With respect to pure magnesium hydroxide powder, the EML composite showed higher reaction rates for dehydration and hydration transformations; further, the EML could dehydrate and hydrate at the same reaction temperature (200 °C). Addition of LiBr was found to decrease the estimated activation energy in the dehydration. The heat output capacity of the EML composite calculated at a hydration temperature of 110 °C was 1405.3 kJ kg^{-1}, which was higher than that of pure MgO. It was established that the newly developed EML composite is a promising candidate for novel chemical heat-storage materials for chemical heat pumps at working temperatures of 200–300 °C.

1. Introduction

Thermal energy storage (TES) is a technology that stocks thermal energy by a storage medium and has a critical importance for transition to and operation of a more efficient, sustainable and low carbon energy system. TES plays a vital role in renewable energy, industrial technologies and waste heat recovery. There are several ways to store the thermal energy by sensible heat, by latent heat, by chemical reactions [1]. Of all these ways, chemical reactions based on solid−gas systems show the highest potential for energy savings. In these systems, heat is stored by way of a reversible chemical

reaction which is carried out in a chemical heat pump (CHP). The CHP is one of the promising technologies and has relatively high-storage density and long-term heat storage ability. In this study, a magnesium oxide/water (MgO/H$_2$O) CHP demonstrated by Kato et al. [2] was examined. It is based on a reversible chemical reaction between MgO and H$_2$O, as shown in the following equation:

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

$$H_2O(g) \leftrightarrow H_2O(l) \quad \Delta H_c = -40.7 \text{ kJ mol}^{-1}$$

where the right-hand side in Eq. (1), *MgO hydration*, is an exothermic reaction corresponding to the heat output operation of the heat pump system, and the left-hand side reaction, *magnesium hydroxide* (Mg(OH)$_2$) *dehydration*, is an endothermic reaction corresponding to

the heat storage operation. The MgO/H$_2$O CHP is able to store waste heat at around 350 °C and to transfer the stored heat at a temperature between 110 and 150 °C. In order to make MgO/H$_2$O CHP a more plausible and attractive alternative for improving the efficiency of industrial processes and solar engineering, some requirements for chemical heat materials used as the storage media must be fulfilled. The chemical heat storage materials firstly need to have a high reaction performance. Secondly, those stably operate in a medium range of temperatures (200−300 °C). And more is the materials must have a high thermal conductivity. Several additional facts need to be considered, such as inexpensive, available in big quantities and compatible with a cost-effective system design. In present work, a new appropriate chemical heat storage material to be used in MgO/H$_2$O CHP that meet those requirements was proposed. A new composite, named EML, was developed by mixing pure Mg(OH)$_2$ with lithium bromide (LiBr) and expanded graphite (EG) which functioned as reactivity and heat transfer enhancers, respectively. Using EG as a material which promotes the thermal conductivity was not new idea and it shared by several working pairs [3,4]. Because the EG is chemically stable and a high thermal conductivity material and therefore, commonly used as a heat transfer enhancer. The first of synthesis of EG-Mg(OH)$_2$ has been reported in 2011 [5]. The EG-Mg(OH)$_2$ composites, denoted as EM, were made of Mg(OH)$_2$ infiltrated in EG matrix and their thermal conductivities were found to be high depending upon the effective material density and compression [6]. However, the EM composites exhibited a tendency for contact instability between two components since Mg(OH)$_2$ and EG are organic or inorganic, respectively. For the first attempt, an approach was made based on the highly hygroscopic property adding LiBr to enhance the reaction performance and increase mold-ability of the EM composites. The LiBr was chosen for incorporation into the EM composites because of its high hygroscopic properties and large negative enthalpy changes caused by dissolution into water. Further, LiBr is a well-known commercial material widely used in absorption heat pumps and air conditioning systems as an absorbent and desiccant, respectively. This study presents the results of experimental studies investigating the effect of LiBr on reactivity enhancement for a chemical heat-storage material by a thermogravimetric method. Kinetic studies of the EML composites are also performed and are discussed in detail on the basis of experimental results. Finally, the heat output capacities of the EML composites for different hydration temperatures are evaluated.

2. Experimental

2.1. Sample preparation

The following materials were purchased and used as received: pure Mg(OH)$_2$ powder (0.07 μm and 99.9%), lithium bromide monohydrate (LiBr·H$_2$O, 99.5%), supplied by Wako Pure Chemical Industries, Ltd and expanded graphite (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 composite as follows: a specified amount of LiBr·H$_2$O was mixed with 200 mL of ethanol (C$_2$H$_6$O, 95%), followed by addition of pure Mg(OH)$_2$ powder into the solution. Next, the mixture was sonicated for 20 min to generate a homogenous solution with sufficient particle dispersion. The flask containing the sonicated solution was then charged with mounted EG and soaked. Subsequently, the excess ethanol in the solution was removed by evaporation under reduced pressures for about 120 min, and the remaining wet product was dried at 120 °C in an oven overnight. During preparation, it was necessary to pay attention and take care to avoid breaking the shape of the graphite, as this is important for composite mold-

ability in terms of heat transfer enhancement. Two indexes of mixing ratios for preparation of EML composite were defined: the first was a mixing mole ratio, α [-], which was defined as the mole ratio between LiBr and Mg(OH)$_2$; the second was a mixing mass ratio, w [−], defined as the mass ratio between EG and Mg(OH)$_2$. Samples tested in this study were as follows: an EML composite having $\alpha = 0.1$, and $w = 0.5$, where the molar ratio between LiBr and Mg(OH)$_2$ was 1:10 and mass ratio between EG and Mg(OH)$_2$ was 1:2, pure Mg(OH)$_2$ powder, and EM composite ($w = 0.5$), which were used as reference materials. It should be noted that the EM composite ($w = 0.5$) contains a similar amount of EG as that of the EML composite ($\alpha = 0.1$, $w = 0.5$), but the absent of LiBr amounts.

2.2. Thermogravimetric measurements

The reactivity of samples was measured using a thermobalance (TG-9600, Ulvac Shinku-Riko Inc). Experimental procedure for thermogravimetric measurements was generally as follows: a cell made of Pt with inner diameter of 7.5 mm and height of 10 mm was initially charged with about 40 mg of sample, and placed in the TG. The cell was purged with Ar prior to the start of the experiment, and a flow rate of 100 mL min^{-1} of Ar was maintained throughout. One experiment cycle consists of primary drying, dehydration, hydration, and secondary drying processes. In a single experiment cycle, the primary drying process involved sample preheating to 110 °C under a flow of Ar to remove physically adsorbed water over 60 min. Next, the temperature was raised by 20 °C min^{-1} to a targeted 300 °C, at which point Mg(OH)$_2$ dehydration proceeded over 120 min. After dehydration completion, the temperature was decreased to 110 °C. Subsequent MgO hydration was achieved by mixing water supplied by a micro-feeder at 37 μL-water min^{-1} and Ar as a carrier gas at 35 mL min^{-1} under a reaction vapor pressure of 57.8 kPa. After the vapor supply was stopped, the sample was kept at 110 °C for 30 min under Ar purge gas at 100 mL min^{-1} to remove physically adsorbed water from the sample during the second drying process. In the dehydration experiments, the sample was dried at 110 °C in 100 mL of purge Ar for 60 min. Then, the temperature was raised from 110 °C to the dehydration temperatures of 200, 220, 240, 270, and 300 °C, respectively, at a heating rate of 20 °C min^{-1}. Then the temperatures were maintained for 300 min. In the hydration experiments, the procedure was same as that during the single cycle of experiment except that hydration temperature of 110 °C was replaced by 130, 150, 170 and 200 °C, respectively. Each measurement was conducted more than three times on new samples in order to determine their reproducibility; mean values are presented as measured results hereafter.

2.3. Reacted mole fraction

The sample mass was observed to change due to the movement of water vapor corresponding to dehydration and hydration, as shown in Eq. (1). This temporal sample mass change was measured continuously by TG analysis as a function of temperature and time. Thus, the reacted mole fraction, x [%], could be determined from following equation:

$$x = \left(1 + \frac{\Delta m_{H_2O} \cdot M_{Mg(OH)_2}}{m_{Mg(OH)_2} \cdot M_{H_2O}}\right) \cdot 100 \qquad (2)$$

where Δm_{H_2O} [g] is the change in the sample mass caused by the reaction, $m_{Mg(OH)_2}$ [g] is the initial charged mass of Mg(OH)$_2$ in the sample, and $M_{Mg(OH)_2}$ and M_{H_2O} [g mol^{-1}] are the molecular masses of Mg(OH)$_2$ and H$_2$O, respectively.