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Application of lithium orthosilicate for high-temperature thermochemical energy storage

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HIGHLIGHTS

- Li_4SiO_4/CO_2 system is proposed for use in chemical heat pump systems at 650 and 700 °C.
- Li_4SiO_4/CO_2 system showed an enough cyclic reaction durability for 5 cycles.
- The energy storage density of Li_4SiO_4 was estimated to be 750 kJ L^{-1} and 780 kJ kg^{-1}.
- It was demonstrated that Li_4SiO_4 could be used as a thermal heat storage material.

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ABSTRACT

A lithium orthosilicate/carbon dioxide (Li_4SiO_4/CO_2) reaction system is proposed for use in thermochemical energy storage (TcES) and chemical heat pump (CHP) systems at around 700 °C. Carbonation of Li_4SiO_4 exothermically produces lithium carbonate (Li_2CO_3) and lithium metasilicate (Li_2SiO_3). Decarbonation of these products is used for heat storage, and carbonation is used for heat output in a TcES system. A Li_4SiO_4 sample around 20 μm in diameter was prepared from Li_2CO_3 and SiO_2 using a solid-state reaction method. To determine the reactivity of the sample, Li_4SiO_4 carbonation and decarbonation experiments were conducted under CO_2 at several pressures in a closed reactor using thermogravimetric analysis. The Li_4SiO_4 sample's carbonation and decarbonation performance was sufficient for use as a TcES material at around 700 °C. In addition, both reaction temperatures of Li_4SiO_4 varied with the CO_2 pressure. The durability under repeated Li_4SiO_4 carbonation and decarbonation was tested using temperature swing and pressure swing methods. Both methods showed that the Li_4SiO_4 sample has sufficient durability. These results indicate that the temperature for heat storage and heat output by carbonation and decarbonation, respectively, could be controlled by controlling the CO_2 pressure. Li_4SiO_4/CO_2 can be used not only for TcES but also in CHPs. The volumetric and gravimetric thermal energy densities of Li_4SiO_4 for TcES were found to be 750 kJ L^{-1} and 780 kJ kg^{-1}, where the porosity of Li_4SiO_4 was assumed to be 59%. When the reaction system was used as a CHP, and heat stored at 650 °C was warmed and output at 700 °C, 14% of the heat supplied by carbonation was needed for self-heating of the material from 650 to 700 °C, and the volumetric and gravimetric thermal energy densities for heat output were calculated as 650 kJ L^{-1} and 670 kJ kg^{-1}, respectively.

1. Introduction

Presently, utilization of high temperature thermal energy is being discussed to solve a global energy and environmental problems in various fields. Actually there are several expected application for high temperature thermal energy, for example, high efficiency power generation, hydrogen production, iron-making, city gas production, etc. In addition, renewable power generation that includes solar and wind energy systems, high temperature gas-cooled reactor (HTGR) and some high-temperature heat processes can produce thermal energy without environmental pollution, and such is expected to be an important sustainable energy system in the future [1–4]. However, these power generation systems have problems with respect to cost, site and fluctuating

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power output. Therefore, in order to realize the future introduction of such energy resources, these issues must be considered.

Thermochemical energy storage (TcES) can be one of the solutions to address this issues [5,6]. TcES uses reversible endothermic and exothermic chemical reactions for heat storage and output, respectively, and it has several advantages, for example, less energy loss during long-term storage, a high thermal storage density, and a constant temperature output owing to chemical equilibrium. TcES can be used in chemical heat pumps (CHPs) [7–9], which increase the temperature of the stored heat by an endothermic reaction that reverses an exothermic reaction. Therefore, integrating TcES with these power plants is expected to provide additional and more flexible options for future power generation.

In TcES, the available temperature range depends on the chemical reaction; therefore, each chemical reaction has to be investigated in various temperature ranges individually. To date, various chemical reactions have been reported in different temperature ranges, for example, inorganic chlorides/ammonia [10–20], inorganic chlorides, bromides or sulfide/water [21–29], metal/hydrogen [30–34] and metal oxide/water [35–38,29,39] for lower than 400 °C. However, for relatively high-temperature TcES, only a few carbonation of metallic oxides (M_xO) such as CaO and PbO has been studied [40–43]. These reactions can be described as the gas–solid reaction in Eq. (1).

$$M_xO(s) + CO_2(g) \rightleftarrows M_xCO_3(s) \tag{1}$$

According to this equation, the equilibrium conditions are determined only by the reaction temperature and CO_2 pressure. Therefore, it should be possible to control the reaction temperature of a CHP system by thermally changing only the CO_2 pressure. The CaO/CO_2 system has reportedly been used as a TcES and CHP material and employed for heat storage at 830 °C and output at around 900 °C for the CO_2 storage reaction [43]. However, there is no reported material that can be used for TcES at around 700 °C, even though this is becoming a very important temperature range for heat utilization in solar thermal power plants, high-temperature gas-cooled reactors, and some high-temperature industrial processes, and for hydrogen production by fuel reforming. Therefore developments of TcES which can be used at around 700 °C have been strongly demanded.

Difficulties of development of TcES for high temperature storage are seemingly due to the peculiar reaction temperature of metallic oxides/CO_2. Fig. 1 shows the equilibrium diagram for carbonation of several alkali and alkaline earth metal oxides. The pressure equilibrium constant for the forward reaction, K_p, is defined as

$$K_p = \frac{1}{P_{CO_2}/P_0} \tag{2}$$

P_{CO_2} : CO_2 pressure [kPa]
P_0 : Standard – state pressure [kPa]

Several K_p values were calculated using a simulation software (HSC chemistry, Outotec) [44]. Each metallic oxide can be used as a TcES material at nearly $-\ln K_p = 0$. Fig. 1 reveals that there is no material available at a working temperature of around 700 °C.

Carbonation of metallic oxides has been investigated for separation of CO_2 gas from the exhaust gas of thermal power plants and high-temperature industrial processes for CO_2 capture and storage and reduction of CO_2 emissions. Nakagawa and Ohashi [45] reported a novel method of CO_2 separation at 680 °C using lithium zirconate (Li_2ZrO_3). Kato and Nakagawa [46] also found that lithium containing a complex oxide can adsorb CO_2 effectively, and moreover can do so at 700 °C, as calculated from the equilibrium diagram (Fig. 2), showing high durability. According to these

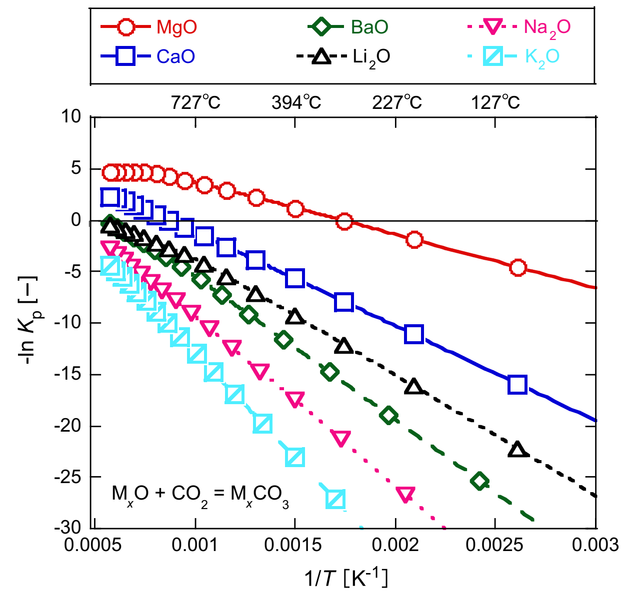

Fig. 1. Equilibrium diagram for carbonation of several alkali and alkaline earth metal oxides [44].

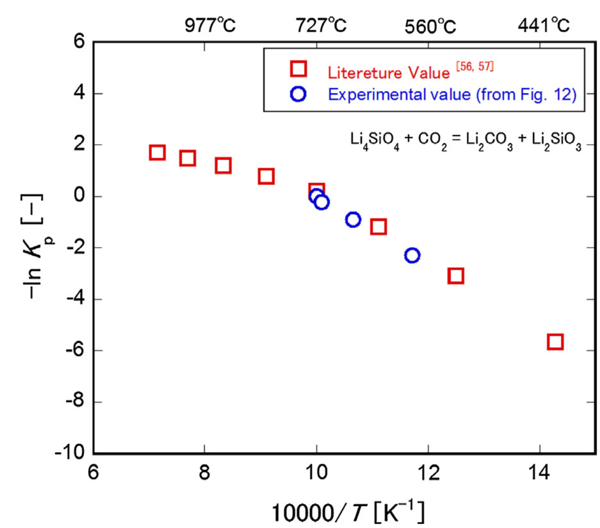

Fig. 2. Relationship between CO_2 pressure and equilibrium temperature.

earlier studies [45,46], the reaction temperature can be reduced by developing a composite material containing metallic oxides. Consequently, various types of metal-containing complex oxides, especially those based on lithium, have been extensively studied for CO_2 separation [47–51]. These are expected to be used not only as CO_2 separators but also TcES materials at relatively high temperatures. However, very few studies have deal with these metal-containing complex oxides for TcES. Thus, developments of these material for TcES have great potential.

To date, many studies of these oxides have been conducted in a flow reactor or under low CO_2 concentration to examine CO_2 separation for power plants and industrial exhaust. However, when we consider their use as a TcES material, it is desirable to use them in a batch reactor under 100% CO_2 concentration. Therefore, in this study, we focused on lithium orthosilicate (Li_4SiO_4), which is one of the best materials for CO_2 separators, according to Eq. (3), for TcES operation at around 700 °C, and developed a candidate Li_4SiO_4 material for TcES.