

Additive Effect on Lithium Silicate Pellets for Thermochemical Energy Storage

Hiroki TAKASU¹, Takuya NIHEI², Seon Tae KIM¹ and Yukitaka KATO¹

¹Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, 2-12-1-N-22 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

²Graduate Major in Nuclear Engineering, Tokyo Institute of Technology, 2-12-1-N-22 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Keywords: Thermochemical Energy Storage, CO₂ Absorption, Metal Oxides, Carbonate Salt

The global increase in energy consumption has caused serious environmental problems, especially CO₂ emissions. In general, CO₂ is produced from the combustion and oxidation reactions at high temperature. The use of thermochemical energy storage is considered an appropriate approach to enhance the utilization of surplus or waste heat from high temperature industrial processes. So far, there are very few reports that have been published for high temperature thermochemical energy storage. In this study, high temperature thermochemical energy storage based on the lithium orthosilicate/carbon dioxide (Li₄SiO₄/CO₂) reaction was developed. A new candidate storage material was fabricated with four different concentrations of the potassium carbonate (K₂CO₃) additive (0, 6, 11, 17, and 33 mol%), in the shape of pellets, from the point of energy density view. On the basis of the results of the carbonation and decarbonation experiments, the highest thermal output and storage densities were recorded for a pellet possessing a 11 mol% concentration of the K₂CO₃ additive. Furthermore, this pellet, LK11, showed cyclic ability with repeat reactions over twenty cycles. Thus, LK11 pellet can be used as a thermochemical storage material because of its ability to store and release heat at high temperatures, ranging from 550 to 700°C.

Introduction

Thermal energy storage is a significant and viable solution to counter serious environmental issues, including global warming and natural source depletion. Thermal energy storage is a technology which is designed to accumulate energy when production exceeds demand, and to make it available at the users' demand. Among thermal energy storage technologies, the thermochemical energy storage (TcES) system is considered to be the most promising, offering several advantages, such as relatively low energy loss during long-term storage and high thermal energy storage density.

At the high temperature of 700°C, the lithium orthosilicate/carbon dioxide (Li₄SiO₄/CO₂) reaction is one candidate of thermochemical energy storages (Takasu *et al.*, 2017). Deployment of this system is considered an appropriate method to enhance the utilization of surplus or waste heat from high temperature industrial processes such as in the ironmaking industry (Maruoka *et al.*, 2004; Zhang *et al.*, 2013; Shigaki *et al.*, 2015), solar power plants (Ervin, 1977; Tian and Zhao, 2013; Carrillo *et al.*, 2019), high-temperature gas-cooled reactors, etc. (Kato *et al.*, 2001; Okazaki *et al.*, 2015; Forsberg *et al.*, 2018).

Thermochemical storage systems based on Li₄SiO₄/CO₂ uses the reversible chemical reaction and sorption to change the temperature level of thermal energy stored by chemical

substances. It is based on the following equilibria:



Li₄SiO₄ can absorb the same amount of CO₂ and produces lithium carbonate (Li₂CO₃) and lithium metasilicate (Li₂SiO₃), and the reaction enthalpy, Δ*H_p*, is around −94 kJ mol^{−1} (Barin, 1995). Even though other metal oxides can react with CO₂ at high temperatures (Kyaw *et al.*, 1996; Kato *et al.*, 1999; Cot-Gores *et al.*, 2012), the reactivity of Li₄SiO₄ is relatively high. In our earlier research work, Li₄SiO₄ was confirmed to have sufficient performance as a TcES material at 700°C (Takasu *et al.*, 2017, 2018). However, the reactivity of Li₄SiO₄ was decreased dramatically at temperatures lower than 680°C. This is caused by the melting temperature of Li₂CO₃ (723°C). Formation of solid Li₂CO₃ and Li₂SiO₃ layers on the unreacted Li₄SiO₄ disturb the CO₂ diffusion and inhibit further reaction. Considering the application for high temperature TcES, reactivity improvement of Li₄SiO₄ is required at especially low temperatures.

The alkali metal carbonates such as potassium carbonates (K₂CO₃) and sodium carbonates (Na₂CO₃) are well-known additives that improve the CO₂ sorption property of Li₄SiO₄ (Yan *et al.*, 2019). For instance, Seggiani *et al.* (2013) reported the sorption performance of Li₄SiO₄ with different ratios (10–30 mass%) of K₂CO₃ and Na₂CO₃, under 4% CO₂ concentration at 580°C and the sample with 30 mass% of K₂CO₃ exhibited higher sorption capacity and durability than pure Li₄SiO₄ (Yan *et al.*, 2019). Yan *et al.* (2019) also investigated the sorption performance of Li₄SiO₄, using a small mix (1–10 mass% and 5–20 mass%) of K₂CO₃ and Na₂CO₃ under

Received on May 29, 2020; accepted on September 16, 2020

DOI: 10.1252/jcej.20we097

Correspondence concerning this article should be addressed to H. Takasu (E-mail address: takasu.h.aa@m.titech.ac.jp).

Table 1 Summary information of prepared pellets

Sample	Molar ratio of Li ₂ CO ₃ :SiO ₂ :K ₂ CO ₃	Mass ratio* [mass%]			Height [mm]	Diameter [mm]	Initial pellet mass [mg]	Pellet mass, m_{pellet} (after pre-treatment) [mg]
		K ₂ O·8TiO ₂	CMC	H ₂ O				
LK0	2.0:1.1:0	10	5	20	4.8±0.3	7.1±0.1	229±8	134±2
LK6	2.0:1.1:0.06	10	5	20	4.6±0.3	7.1±0.1	230±11	134±4
LK11	2.0:1.1:0.11	10	5	20	4.5±0.3	7.1±0.1	238±5	134±3
LK17	2.0:1.1:0.17	10	5	20	4.3±0.2	7.1±0.1	235±6	134±2
LK33	2.0:1.1:0.33	10	5	20	4.0±0.2	7.1±0.1	238±4	135±5

*Mass ratio to the total mass of Li₂CO₃ and SiO₂ in the mixture

15% of CO₂ at 550°C. It was confirmed that both additives enhanced reaction rates and capacities of Li₄SiO₄, and the sample with 5 mass% of K₂CO₃ and 10 mass% of Na₂CO₃ were the optimum addition ratios under the measurement conditions. Although they confirmed the reactivity enhancement with the alkali metal carbonates, the optimum additive ratio is likely to change depending on the measurement conditions.

Especially for its utilization as a high temperature TcES, reactivities of Li₄SiO₄ under high concentrations of CO₂ needs to be investigated. In our previous work, the reactivity enhancement of K₂CO₃ was also confirmed with Li₄SiO₄ pellets at 600–700°C (Kim *et al.*, 2019a, 2019b). However, the reactivities of Li₄SiO₄ with different ratios of K₂CO₃ additives had not been completed under high concentrations of CO₂. Therefore, in this study, Li₄SiO₄ tablets with different ratios of K₂CO₃ additives were prepared and the reactivities of these pellets were compared between 550–700°C. Also, the durability of a Li₄SiO₄ pellet was investigated at 600°C for 20 cycles.

1. Experimental

1.1 Material

Initially, the initial materials of lithium carbonate (Li₂CO₃, 99.0%, Wako Pure Chemical Industries, Ltd.), silicon dioxide (SiO₂, 99.0%, Wako Pure Chemical Industries, Ltd.), and potassium carbonate (K₂CO₃, 99.0%, Wako Pure Chemical Industries, Ltd.) were mixed with mortar and pestle. The mixing molar ratios of Li₂CO₃/SiO₂/K₂CO₃ were 2.0:1.1:0, 0.06, 0.11, 0.17, and 0.33.

Next, potassium titanate fiber (K₂O·8TiO₂, TISMO-D, Otsuka Chemical Co., Ltd.), carboxymethyl cellulose (CMC, CMF-7, AS ONE), and pure water were added to the mixture as a reinforcing agent and a granulation binder, and it was also mixed with a mortar and pestle. The additive amounts of potassium titanate fiber, CMC and water were 1/10, 1/20, and 1/5 as much as the total mass of Li₂CO₃ and SiO₂ in the mixture. Around 250 mg of powder was put into a mold (ϕ : 7.0 mm) and compressed with 15 kN for 3 min by a table press (TB-20H, Sansho Industry Co., Ltd.). Finally, lithium silicate pellets were obtained. According to the ratio of K₂CO₃, each pellet was named LK0, LK6, LK11, LK17 and LK33, and the basic information of these pellets is summarized in **Table 1**.

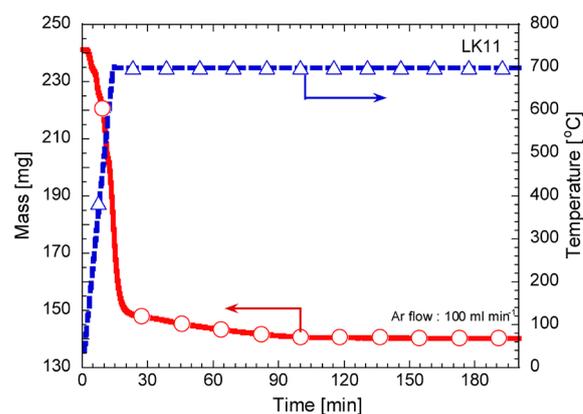


Fig. 1 Mass change of LK11 under thermal treatment under Ar flow

1.2 Pre-treatment

All pellets were subjected to thermal treatment to synthesize lithium orthosilicate and remove residues, as pre-treatment. A pellet was heated up to 700°C from room temperature under Argon (Ar) flow, and was kept for 90 min at 700°C. **Figure 1** shows the mass change of LK11 during thermal treatment. Initially, a rapid mass drop was observed with increasing temperature. Hereafter, a modest decline was observed for around 90 min after reaching 700°C. Afterward, almost no change was observed. Similar behavior was observed for all pellets. These results confirmed that thermal treatment at 700°C for 90 min was suitable as a pre-treatment for these silicate pellets. The mass of the pellet after pre-treatment, m_{pellet} , was measured and summarized in **Table 1**.

1.3 Reactivity measurement

After pre-treatment, reactivity measurement for carbonation and decarbonation was conducted at 4 different temperatures (550, 600, 650, and 700°C), using a thermobalance (TG-9600S; Ulvac Shinku-Riko Inc.). For taking this measurement, the thermobalance was kept at the target temperature for 360 min. For carbonation and decarbonation, 100 mL min⁻¹ (STP) of CO₂ and Ar were supplied to the pellet for 180 min. Mass changes of pellet were measured by the thermobalance, and the reacted CO₂ amount, n_{CO_2} [mol/kg_{pellet}], was calculated as in Eq. (2).

$$n_{\text{CO}_2} = \frac{\Delta m}{M_{\text{CO}_2} \cdot m_{\text{pellet}}} \quad (2)$$

Herein, Δm [kg], M_{CO_2} [kg/mol], and m_{pellet} [kg] indicate the

mass change, the molar mass of CO_2 , and mass of the pellet, respectively.

1.4 Durability measurement

After pre-treatment, durability measurement was conducted with LK11 at 600°C for 20 cycles. For carbonation and decarbonation, 100 mL min^{-1} (STP) of CO_2 and Ar was supplied to the pellet each for 90 min. The thermal output and storage density, $q_{\text{output}}, q_{\text{storage}}$ [$\text{kJ/kg}_{\text{pellet}}$], were calculated from the CO_2 amount absorbed and desorbed, respectively, as shown in Eq. (3).

$$q_{\text{output, storage}} = -\Delta H_r \cdot \Delta n_{\text{carb, decarb}} \quad (3)$$

Herein, $\Delta n_{\text{carb, decarb}}$ indicates the change of the reacted CO_2 amount for each carbonation and decarbonation process, and is defined as shown in Eqs. (4), (5).

$$\Delta n_{\text{carb}} = n_{\text{carb, f}} - n_{\text{carb, i}} \quad (4)$$

$$\Delta n_{\text{decarb}} = n_{\text{decarb, i}} - n_{\text{decarb, f}} \quad (5)$$

Herein, $n_{\text{carb, i}}, n_{\text{decarb, i}}, n_{\text{carb, f}}$ and $n_{\text{decarb, f}}$ refer to values of n at the beginning and the end of the carbonation and decarbonation processes.

2. Results and Discussion

The changes in the reacted CO_2 amount resulting from the carbonation and decarbonation processes for LK0, LK6, 11, 17 and 33 pellets measured at 550, 600, 650 and 700°C

are presented in Figure 2. During carbonation, LK6, LK11, and LK17 showed large changes in terms of the reacted CO_2 amount, compared to the LK0 pellet, which indicates that the K_2CO_3 additive in LK6, 11, and 17 was employed for reactivity enhancement. In other words, the K_2CO_3 additive plays a significant role in producing a eutectic salt with Li_2CO_3 , which is covered with unreacted Li_4SiO_4 during carbonation. As a consequence, the melting point becomes lower than that of pure Li_2CO_3 , thereby accelerating CO_2 diffusion through this eutectic liquid. As a result, carbonation reactivity is enhanced. However, LK33 showed inferior performance when compared with LK6, LK11, and LK17 at all temperatures. This result implies that excessive K_2CO_3 additives impede the reactivity of Li_4SiO_4 .

In decarbonation, all pellets desorbed over 90% of CO_2 , which were absorbed in carbonation at 700 and 650°C , as shown in Figure 2(a) and (b). Considering the reactivity at different temperatures, a trend was observed in the pellets with less K_2CO_3 additive. A large change of the reacted CO_2 amount was observed at $650, 600$ and 550°C , at different temperatures, a trend was observed in the pellets with less K_2CO_3 additive. A large change of the reacted CO_2 amount was observed at $650, 600$ and 550°C , as shown in Figure 2(b)–(d). In addition, LK33 was confirmed to perform below par during decarbonation, as compared to other pellets at $650, 600$ and 550°C . According to a phase-diagram of K_2CO_3 – Li_2CO_3 (CRCT-ThermoFact.inc and GTT-Technologies, 2018), the melting temperature of salt liquid tends to increase rap-

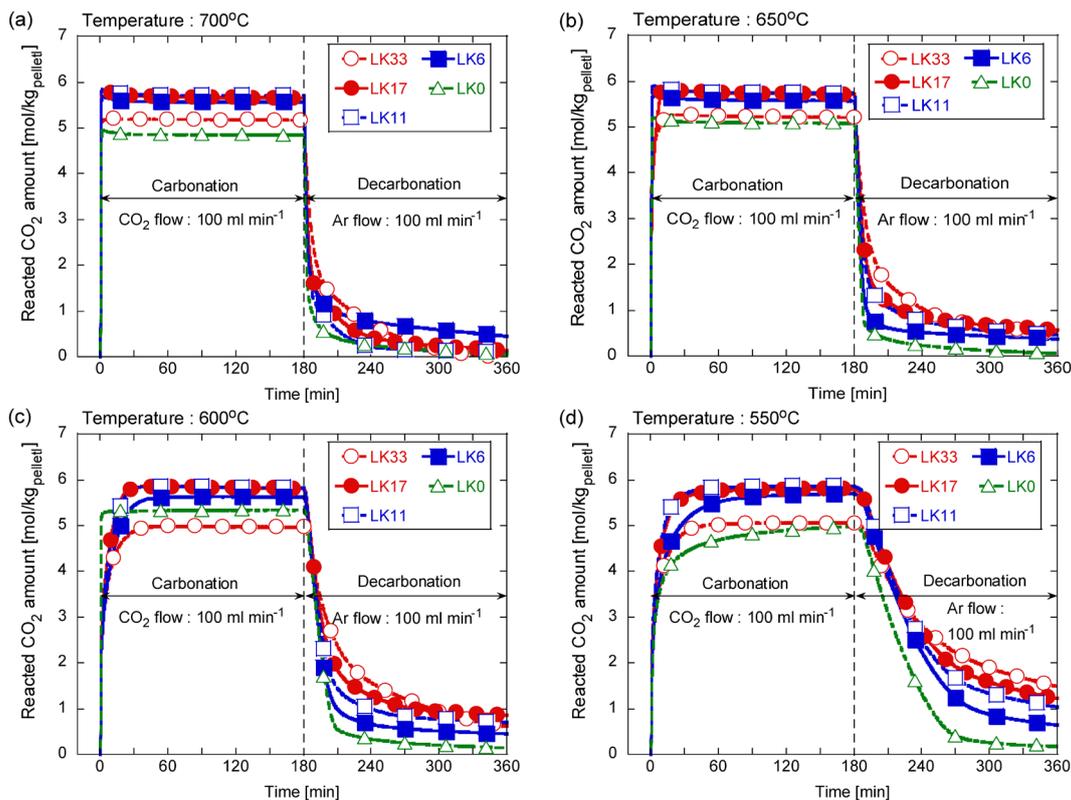


Fig. 2 Carbonation and decarbonation behavior of LK samples at (a) 700, (b) 650, (c) 600, and (d) 550°C under 100 kPa of CO_2 ; carbonation process: 100 mL min^{-1} of CO_2 flow for 180 min; decarbonation process: 100 mL min^{-1} of Ar flow for 180 min

idly corresponding to increasing ratio of K_2CO_3 . Thus, excess K_2CO_3 seemingly remains as solid state in the pellets and it may disturb reactions especially at low temperature.

These results indicated that proper amounts of K_2CO_3 additive can enhance carbonation. Also, excessive K_2CO_3 can impede the reactivity of carbonation, as well as decarbonation, especially at low temperatures.

To further investigate the effects of the concentration of K_2CO_3 additive, the change in the reacted CO_2 amount in 60 min for carbonation and decarbonation processes of LK pellets were evaluated and shown in Figure 3.

As shown in Figure 3(a), it was found that the change in the reacted CO_2 amount in carbonation, Δn_{carb} , initially increased with increasing concentrations of K_2CO_3 additive. It reached its maximum value at LK11 and LK17, and then decreased again regardless of the carbonation temperature. The maximum value of Δn_{carb} was attained by the LK11 pellet, including 11 mol% of K_2CO_3 additive to Li_4SiO_4 . For instance, LK11 pellet showed Δn_{carb} of 5.73, 5.76, 5.86, and 5.84 $mol\ kg_{pellet}^{-1}$, at 700, 650, 600 and 550°C, respectively.

Figure 3(b) shows the change in the reacted CO_2 amount in decarbonation, Δn_{decarb} , of LK pellets, calculated based on the decarbonation data at 700, 650, 600, and 550°C, for the first 60 min of decarbonation. As observed from the com-

parison figure, two different trends were seen, depending on the decarbonation temperature. At lower temperature ranges (550–600°C), the heat storage density kept decreasing when the concentration of K_2CO_3 additive varied between 0 and 33. Conversely, at higher temperature ranges (650–700°C), the Δn_{decarb} initially increased with the increase in the concentration of K_2CO_3 additive, after which, it reached the maximum value. Hereafter, it started decreasing again. At temperature of 650°C, a maximum value of 5.05 $mol\ kg_{pellet}^{-1}$ was recorded for the LK6 pellet, having 6 mol% of K_2CO_3 additive. When the temperature was increased from 650 to 700°C, the maximum value shifted, and a 5.49 $mol\ kg_{pellet}^{-1}$ of Δn_{decarb} was found for the LK11 pellet, possessing 11 mol% of the K_2CO_3 additive to Li_4SiO_4 .

On the basis of the results derived from the changed CO_2 amount of LK pellets, 11 mol% concentration of K_2CO_3 additive would be the optimum value to fabricate high performance storage materials.

The cycle ability of the LK11 pellet (including 11 mol% concentration of K_2CO_3 additive) was explored, and the results are shown in Figure 4.

The carbonation and decarbonation behaviors measured at 600°C are shown in Figure 4(a). It was observed that carbonation and decarbonation occurred for each cycle, and

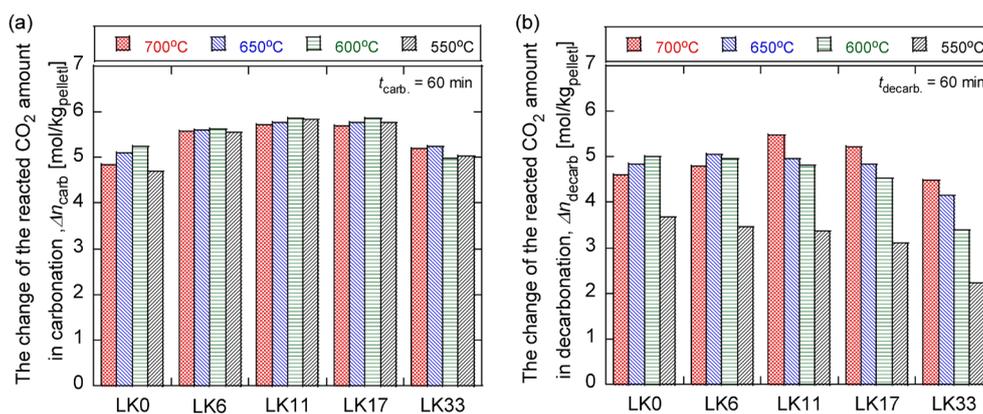


Fig. 3 Dependency of K_2CO_3 additive on the change of the reacted CO_2 amount for (a) carbonation and (b) decarbonation process of LK samples for 60 min at 700, 650, 600, and 550°C

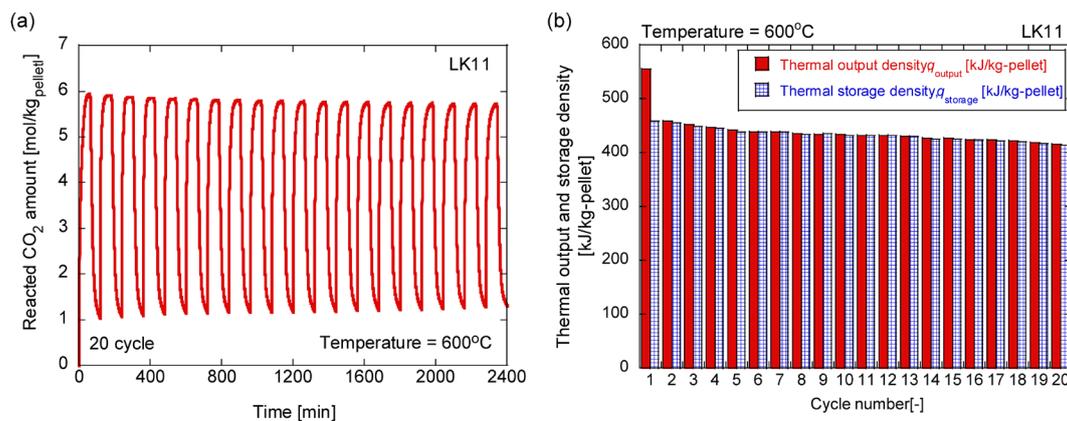


Fig. 4 (a) The reacted CO_2 amount and (b) thermal output and storage density of LK11 on the 20-cycle experiment at 600°C; carbonation process: $100\ mL\ min^{-1}$ of CO_2 flow for 90 min; decarbonation process: $100\ mL\ min^{-1}$ of Ar flow for 90 min

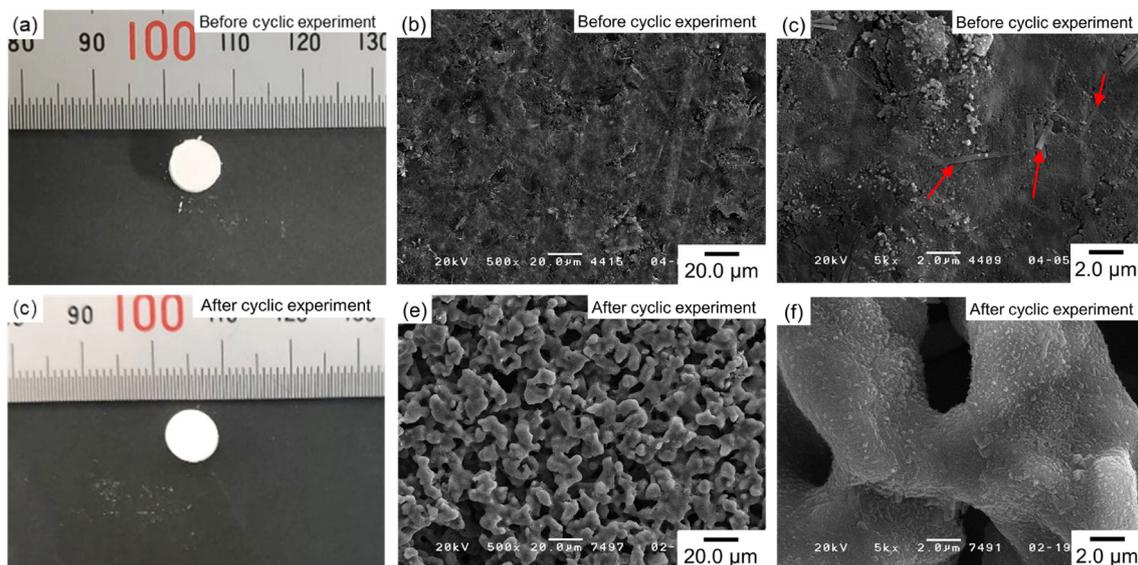


Fig. 5 Images of top pellet surface and SEM images of LK11 (a–c) before and (c–f) after cycle experiment

no significant decrease in reactivity was found during 20 cyclic experiments. Therefore, thermal output and storage densities, q_{output} and q_{storage} , were determined for each cycle, as shown in Figure 4(a). The results are presented in Figure 4(b). It was found that the value of q_{output} storage exceeded 550 kJ kg^{-1} in the first cycle. Then, it decreased slightly between the 2nd and 20th cycles.

The reduction in carbonation and decarbonation processes was less than approximately 11%. On the 20th cycle, the LK11 pellet showed q_{output} and q_{storage} of both $410 \text{ kJ kg}_{\text{pellet}}^{-1}$. This result showed that the LK11 pellet was able to withstand repetitive cyclic reactions without significant failures.

Figure 5(a) and (c) gives the images of the top pellet surfaces, and SEM images of LK11 before and after the cyclic experiment. As illustrated in Figure 5(a) and (c), no significant difference, such as cracks or structural changes, were observed. In addition, the height and diameter of LK11 after the cycle experiment were 4.5 and 7.2 mm, respectively, and thus, no volume change was observed. As a consequence, further characterization on the surfaces of LK11 were done by using the scanning electron microscope (SEM). Figure 5(b), (c), (e), and (f) presents images of SEM at magnifications of $\times 500$ and $5k$, respectively, before and after the cyclic experiment. As presented in Figure 5(b) and (c), fresh LK11 pellet showed a dense structure, with the presence of some potassium titanate fibers, which could be seen particularly at high magnification of $\times 5k$, indicated by the arrow in the figure. On the other hand, the morphology was changed from dense to porous after the cyclic experiment. The potassium titanate fiber was not observed on the surface of the used pellet, as shown in Figure 5(e) and (f). It is assumed that the repetitive liquefaction and solidification of the eutectic salt caused the microstructure change, owing to CO_2 diffusion. To add to that, the tubular fillers also lead to the development of the porous structure.

Conclusions

In this study, the effects of the concentration of the K_2CO_3 additive on carbonation and decarbonation behaviors were investigated using the thermogravimetric approach, and the experimental results were discussed. The pellets with five different concentrations of K_2CO_3 additive (0, 6, 11, 17 and 33 mol%) were investigated. A 11 mol% concentration of K_2CO_3 additive would be the optimum value to fabricate high performance storage materials, based on the results derived from the carbonation and decarbonation experiments. The Δn_{carb} values of LK11 were 5.73, 5.76, 5.86, and $5.84 \text{ mol kg}_{\text{pellet}}^{-1}$ at 700, 650, 600 and 550°C , respectively. As for the cycle experiment, LK11 showed repetitive cyclic durability without significant failures, with less than 11% of degradation between the 2nd and 20th cycle. On the 20th cycle, the LK11 pellet showed a similar q_{output} and q_{storage} as the $410 \text{ kJ kg}_{\text{pellet}}^{-1}$. After the cyclic experiment, the LK11 pellet maintained the macrostructure and no significant change on the surface was found. According to the SEM characterization, the fresh pellet had a dense morphology. However, it became porous after the cyclic experiment. Therefore, the LK11 pellet showed superior performance, and is a promising candidate for thermochemical energy storage at high temperatures above 600°C .

Literature Cited

- Barin, I.; Thermochemical Data of Pure Substances 3rd ed., pp. 404–985, VCH Publishers, Inc., Weinheim, U.S.A. (1995)
- Carrillo, A. J., J. González-Aguilar, M. Romero and J. M. Coronado; “A Review on High Temperature Thermochemical Heat Storage Systems and Materials,” *Chem. Rev.*, **119**, 4777–4816 (2019)
- Cot-Gores, J., A. Castell and L. F. Cabeza; “Thermochemical Energy Storage and Conversion: A-State-of-the-Art Review of the Experimental Research under Practical Conditions,” *Renew. Sustain. Energy Rev.*, **16**, 5207–5224 (2012)

- CRCT-ThermoFact.inc and GTT-Technologies; FactSage 7.2, www.factsage.com (2018)
- Ervin, G.; "Solar Heat Storage Using Chemical Reactions," *J. Solid State Chem.*, **22**, 51–61 (1977)
- Forsberg, C., S. Brick and G. Haratyk; "Coupling Heat Storage to Nuclear Reactors for Variable Electricity Output with Baseload Reactor Operation," *Electr. J.*, **31**, 23–31 (2018)
- Kato, Y., N. Harada and Y. Yoshizawa; "Kinetic Feasibility of a Chemical Heat Pump for Heat Utilization of High-Temperature Processes," *Appl. Therm. Eng.*, **19**, 239–254 (1999)
- Kato, Y., M. Yamada, T. Kanie and Y. Yoshizawa; "Calcium Oxide/Carbon Dioxide Reactivity in a Packed Bed Reactor of a Chemical Heat Pump for High-Temperature Gas Reactors," *Nucl. Eng. Des.*, **210**, 1–8 (2001)
- Kim, S. T., C. Kurahashi, H. Hoshino, C. Takahashi, Y. Tamura, H. Takasu, S. Saito, M. Kurihara and Y. Kato; "Thermal Driving Demonstration of $\text{Li}_4\text{SiO}_4/\text{CO}_2/\text{Zeolite}$ Thermochemical Energy Storage System for Efficient High-Temperature Heat Utilizations," *ISIJ Int.*, **59**, 721–726 (2019a)
- Kim, S. T., T. Nihei, C. Kurahashi, H. Hoshino, H. Takasu and Y. Kato; "Kinetic Study of Lithium Orthosilicate Pellets for High-Temperature Chemical Heat Pumps," *Energy Storage*, **1**, 1–9 (2019b)
- Kyaw, K., M. Kanamori, H. Matsuda and M. Hasatani; "Study of Carbonation Reactions of Ca–Mg Oxides for High Temperature Energy Storage and Heat Transformation," *J. Chem. Eng. Japan*, **29**, 112–118 (1996)
- Maruoka, N., T. Mizuochi, H. Purwanto and T. Akiyama; "Feasibility Study for Recovering Waste Heat in the Steelmaking Industry Using a Chemical Recuperator," *ISIJ Int.*, **44**, 257–262 (2004)
- Okazaki, T., Y. Shirai and T. Nakamura; "Concept Study of Wind Power Utilizing Direct Thermal Energy Conversion and Thermal Energy Storage," *Renew. Energy*, **83**, 332–338 (2015)
- Seggiani, M., M. Puccini and S. Vitolo; "Alkali Promoted Lithium Orthosilicate for CO_2 Capture at high Temperature and Low Concentration," *Int. J. Greenh. Gas Control*, **17**, 25–31 (2013)
- Shigaki, N., H. Tobo, S. Ozawa, Y. Ta and K. Hagiwara; "Heat Recovery Process from Packed Bed of Hot Slag Plates," *ISIJ Int.*, **55**, 2258–2265 (2015)
- Takasu, H., J. Ryu and Y. Kato; "Application of Lithium Orthosilicate for High-Temperature Thermochemical Energy Storage," *Appl. Energy*, **193**, 74–83 (2017)
- Takasu, H., S. Funayama, N. Uchiyama, H. Hoshino, Y. Tamura and Y. Kato; "Kinetic Analysis of the Carbonation of Lithium Orthosilicate Using the Shrinking Core Model," *Ceram. Int.*, **44**, 11835–11839 (2018)
- Tian, Y. and C. Y. Zhao; "A Review of Solar Collectors and Thermal Energy Storage in Solar Thermal Applications," *Appl. Energy*, **104**, 538–553 (2013)
- Yan, X., Y. Li, X. Ma, J. Zhao and Z. Wang; "Performance of Li_4SiO_4 Material for CO_2 Capture: A Review," *Int. J. Mol. Sci.*, **20**, 928 (2019)
- Zhang, H., H. Wang, X. Zhu, Y. J. Qiu, K. Li, R. Chen and Q. Liao; "A Review of Waste Heat Recovery Technologies towards Molten Slag in Steel Industry," *Appl. Energy*, **112**, 956–966 (2013)