

Acceleration Effect of Ternary Carbonate on CO₂ Absorption Rate in Lithium Zirconate Powder

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3元系炭酸塩がリチウムジルコネートのCO₂吸収速度に与える加速効果

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Acceleration effect of the ternary carbonate of Li/Na/K on the CO₂-absorption rate of lithium zirconate was studied. Potassium carbonate additive in lithium zirconate powder clearly produces the absorption-rate acceleration as a result of the formation of the binary carbonate of Li/K, which melts at around 500°C. The experimental results obtained revealed that the lithium zirconate powder with the ternary carbonate of Li/Na/K (ternary-type lithium zirconate) shows a more accelerated absorption rate at 500°C, and particularly at 450°C, than does the powder with the binary carbonate of Li/K (binary-type lithium zirconate). At 500°C, the reaction-yield range of CO₂ absorption by a ternary-type lithium zirconate, which shows complete melting of the carbonate formed during the reaction, is 2.3 times as long as that by a binary-type. Furthermore, even at 450°C, this ternary type has the range of the complete melting, which is as long as that by the binary-type at 500°C, whereas the binary-type does not have the range. The difference of the acceleration effect between the ternary and the binary carbonate was attributed to the difference of the length of this reaction-yield range.

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1. Introduction

Carbon dioxide (CO₂) emissions, mostly results of fossil fuel combustion, are thought to cause climate changes. Among the various technologies for reduction of these emissions, CO₂ segregation is expected to have an immediate beneficial impact. As previously reported, power plants are possible target for large-scale CO₂ segregation.^{1)–3)} Moreover, it is more advantageous to segregate CO₂ at the fuel reforming process than from flue gas of the plant, since the CO₂ partial pressure in the former case is high and the gas volume is small.⁴⁾ However, all CO₂ segregation methods currently in practical use are not applicable for this purpose, because their poor heat tolerance makes them unsuitable for use at the reforming process.

Considering these difficulties, we previously reported a lithium zirconate (Li₂ZrO₃) absorbent which reacts with CO₂ at around 500°C and emits CO₂ at above 700°C.⁵⁾ Its

reversible reaction is represented by Eq. (1).



It is thought to be applicable for CO₂ segregation at the fuel reforming process which proceeds at around 500°C. The lithium zirconate absorbent contains potassium carbonate (K₂CO₃) additive in order to accelerate the reaction rate between lithium zirconate and CO₂. Figure 1 shows a model^{5),6)} for this reaction. CO₂ reacts with lithium oxide (Li₂O) which is contained in lithium zirconate. Lithium carbonate (Li₂CO₃) is thus produced on the surface by the reaction, forming a layer around the absorbent particles. Lithium zirconate finally changes into zirconia (ZrO₂). Since the melting point of lithium carbonate is 730°C, which is much higher than the absorption temperature, the solid layer of lithium carbonate hinders further reaction in the absence of potassium carbonate. On the contrary, lithium zirconate

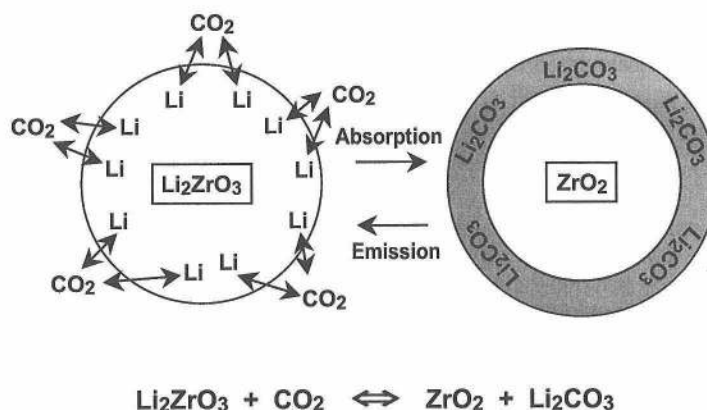


Fig. 1. A model for the reaction of lithium zirconate with CO₂.

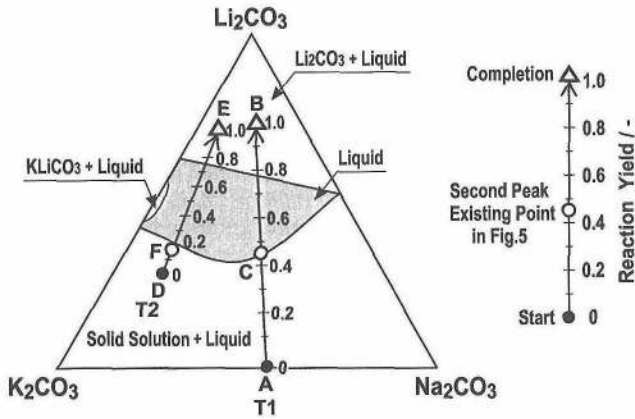


Fig. 6. Changes in carbonate composition during absorption. (Samples (T1) and (T2)).

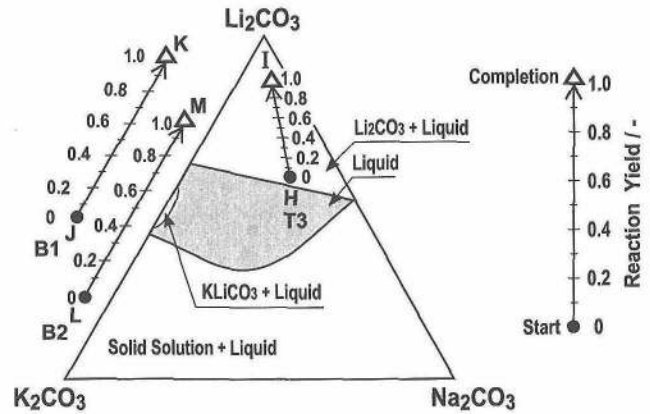


Fig. 7. Changes in carbonate composition during absorption. (Samples (T3), (B1) and (B2)).

sample carbonate.

On the contrary, the composition changes of Samples (B1), (B2) and (T3) show different locus of phase changes from those samples, as shown in Fig. 7. The extra carbonate of Sample (T3) includes too much lithium carbonate to cause complete melting of sample carbonates. Besides, sample carbonates of Samples (B1) and (B2) melt completely only in the narrow range of reaction yield, because the total-liquid-phase region is not obvious in the Li/K binary locus at 500°C. After all, the loci of phase change are generated by the composition of extra carbonate, which is in excess of lithium zirconate synthesis. It is noteworthy that the composition of the extra carbonate in a sample is a significant factor for accelerating the CO₂ absorption. On the basis of these findings, we assumed two criteria for the proper composition of extra carbonate. Firstly, from the viewpoint of quick absorption, the extra carbonate should have the composition, which is beneficial for achieving lower melting point of carbonate mixture. Figure 2 shows that the composition, which is an almost equal mixture of potassium and sodium carbonate, has lower melting point. This composition is also beneficial for maintaining the complete melting condition with long duration. Wide compositional range of total-liquid-phase provides wide tolerance for the reaction yield. Secondly, in order to cause the second peak, the extra carbonate should pass the total-liquid-phase region due to the change in carbonate during the reaction. Figure 2, therefore, shows that lithium zirconate, used as a CO₂ absorbent at 500°C, should have a composition of extra carbonate, which contains less than half mol ratio of lithium carbonate. In order to confirm these assumptions, ternary-type lithium zirconate powder which satisfies the criteria was compared with binary-type. Figures 8(a) and (b) show the difference of weight changes between Samples (B1) and (T1) during the reaction at 500°C and 450°C. Since the weight change indicates exact CO₂-absorbing capacity of a unit-weight sample, which is useful to evaluate industrial value, weight change was adopted instead of reaction yield for the vertical axis in Figs. 8(a) and (b). Sample (T1) is a typical example which clearly satisfies the criteria mentioned above. Since one mol of Li₂ZrO₃ is produced from one mol of ZrO₂ and one mol of Li₂CO₃ as shown in Eq. (2), extra carbonate of Sample (B1) with one mol Li₂ZrO₃ is estimated on the basis of Table 1 as 0.1 mol of Li₂CO₃ and 0.12 mol of K₂CO₃, whereas that of Sample (B2) is estimated as 0.1 mol of Li₂CO₃ and 0.40 mol of K₂CO₃. Because Sample (B1) contains less amount of extra carbonate and more of lithium zirconate in a unit-weight than Sample (B2), Sample (B1) is

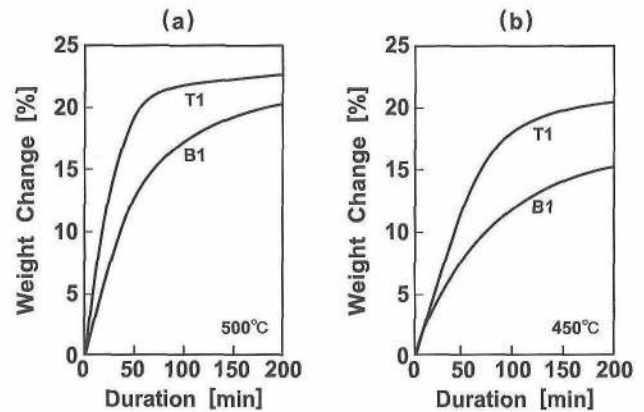


Fig. 8. Weight changes of Samples (T1) and (B1). (a) at 500°C, (b) at 450°C. (CO₂: 20 vol%, total pressure: 0.1 MPa).

advantageous since it indicates a larger value of weight change than does Sample (B2). Analogous to Fig. 5, Sample (T1) shows faster weight change than Sample (B1) at 500°C. Furthermore, the difference of weight change becomes more drastic at 450°C.

Figure 9, based on Figs. 2, 6 and 7, shows relationship between the changes in sample carbonate composition of Samples (T1) and (B1) during absorption and total-liquid-phase region at 500°C and 450°C. At 500°C, the reaction-yield range of Sample (T1), which shows complete melting of the carbonate, is the reaction yield from 0.45 to 0.77. The length is 2.3 times as long as that of Sample (B1), the reaction yield from 0.23 to 0.37. Furthermore, even at 450°C, the range of Sample (T1) is the reaction yield from 0.53 to 0.67, which is as long as that of Sample (B1) at 500°C, whereas Sample (B1) does not show the complete melting and the length is zero. The difference of the acceleration effect was attributed to the difference in this length of reaction-yield range, which shows complete melting of the carbonates. As shown in Figs. 2, 6 and 7, Sample (T1) has the extra carbonate which causes the complete melting during CO₂ absorption even at 400°C, whereas the carbonate of Sample (B1) scarcely melts below 500°C. Because of this difference in the temperature of the complete melting, *viz.* 100°C, it is believed that Sample (T1) is more advantageous as a CO₂ absorbent than is Sample (B1), and especially so at around

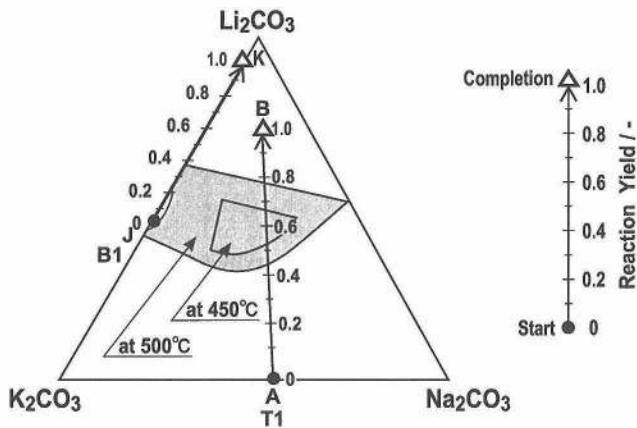


Fig. 9. Relationship between the changes in carbonate composition of Samples (T1) and (B1) and total-liquid-phase region at 500°C and 450°C.

450°C.

4. Conclusion

All these experimental results indicate that the ternary carbonate, consisting of lithium carbonate, sodium car-

bonate and potassium carbonate is especially beneficial for accelerating the reaction between lithium zirconate and CO_2 . In particular, the samples with extra carbonate, which causes complete melting of sample carbonate, have a second peak in reaction rate and indicate faster absorption rate than the sample with potassium carbonate alone. On the basis of the phase diagram of ternary carbonate, it was suggested that the wide compositional range for the complete melting is beneficial for avoiding the appearance of solid carbonate which hinders the absorption. We conclude that the difference in the temperature of the complete melting between binary and ternary carbonate, viz. 100°C, provides a drastic improvement in acceleration respecting CO_2 absorption.

References

- 1) Ogawa, K., *J. Japan Power Association*, 241, 8–19 (1997) [in Japanese].
- 2) Desideri, U. and Paolucci, A., *Energy Conversion & Management*, 40, 1899–915 (1993).
- 3) Riemer, P., *Energy Conversion & Management*, 37[6–8], 665–70 (1996).
- 4) Matsubashi, R., Ishitani, H. and Pak, P. S., *IEE Japan*, 112–B(6), 531–37 (1992) [in Japanese].
- 5) Nakagawa, K. and Ohashi, T., *J. Electrochem. Soc.*, 145, 1344–46 (1998).
- 6) Ohashi, T. and Nakagawa, K., "Materials Research Society Symposium," Vol. 547, Boston, USA (1998) p. 249.
- 7) Pelton, A. D., Bale, C. W. and Lin, P. L., *Canadian Journal of Chemistry*, 62, 457–74 (1984).