

Novel Ceramic Membrane for High Temperature
Carbon Dioxide Separation

Technical Progress Report (Semi-Annual)

03/01/01

08/31/01

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September 2001

DE-FG26-00NT40824

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ABSTRACT

The Objective of this research program is to develop a dense, non-porous ceramic membrane for separation of carbon dioxide from flue gas at high temperatures (400-600 °C). The research has been focused on addressing several fundamental issues of lithium zirconate (Li_2ZrO_3). In the 2nd half research, we conducted various kinds of experiments to understand the CO_2 sorption/desorption mechanism on the pure and modified Li_2ZrO_3 with the help of TGA, DSC-TGA and XRD. DSC-TGA results suggest that the melting of Li/K carbonates mixture may play an important role in rapid CO_2 sorption in the case of modified lithium zirconate. The CO_2 desorption experiments show that CO_2 desorption from the modified lithium zirconate follows the same mechanism as that from the pure lithium zirconate. This is different from the CO_2 adsorption on the pure and modified lithium zirconates.

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INTRODUCTION

Carbon dioxide is produced in many industrial applications such as electrical generation by burning coal. For example, flue gas from conventional coal-burning power plants typically contains about 13% carbon dioxide, 73% nitrogen, 10% water, 3% oxygen and less than 1% various pollutants. The key to the sequestration of carbon dioxide is to separate carbon dioxide from the flue gas [1]. The flue gas from the coal-burner is hot and its temperatures vary from a few hundreds to about a thousand degrees Celsius depending on the specific locations in the flue gas line in the coal-burning power plant. In many cases it is highly desirable to separate CO₂ from flue gas at a high temperature (for example, around 400 °C after the economizer) without cooling the flue gas to room or even lower temperature [2]. The high temperature CO₂ separation process would produce concentrated, warm CO₂ which can be subsequently used directly as a feedstock for chemical synthesis of fuels (e.g., methanol or chemicals) [1]. These synthesis reactions are usually conducted at high temperatures (e.g., 600-800 °C for CO₂ methane reforming reaction).

The existing separation technologies are not able to separate carbon dioxide over other small gases such as nitrogen or hydrogen at high temperatures. Two relative new separation methods are adsorption and membranes. The adsorption process is operated in the batch mode, requiring pressure or temperature swing in order to make the process continuous. Various adsorbents, such as zeolites and carbons, have been studied for many years for use in adsorption processes for separation of CO₂ from gas mixture [3, 4]. However, none of these sorbents can be used to separate CO₂ at high temperatures [4].

Membrane separation is a continuous, steady state process, making it particularly useful for separation of high throughput gas stream. The membrane process for carbon dioxide separation is driven by the partial pressure gradient of carbon dioxide [6]. For separating carbon dioxide from flue gas, this driving force can be provided by feeding flue gas at a high pressure to the feed side or evacuating the permeate side of the membrane module. A combination of the both can be also used to provide the driving force for the membrane separation process. Membrane process is generally more energy efficient and easier to operate than the adsorption process. But it is more difficult to prepare a good quality, highly CO₂ permeable and selective membrane than a similar sorbent.

Many microporous inorganic membranes developed recently show good perm-selectivity for carbon dioxide over nitrogen at low temperatures. This selectivity is however lost at temperatures above 300 °C due to the specific transport mechanism inherent to the microporous membranes. Therefore, following the strategy employed in development of the inorganic membrane for oxygen and nitrogen separation, we proposed to develop a non-porous ceramic membrane for separation of carbon dioxide from flue gas at high temperatures. In this study, we focused on lithium zirconate as a potential material for making dense ceramic membrane for carbon dioxide separation.

EXECUTIVE SUMMARY

Development of membrane or adsorbent for separation of carbon dioxide from various gas streams at high temperatures (400-700 °C) is very important to the reduction of the carbon dioxide emission to the atmosphere and also the use of the separated carbon dioxide subsequently as a feedstock for chemical synthesis of fuels (e.g., methanol or chemicals). Various adsorbents for selective sorption of CO₂ have been studied for many years. For the past few years development of inorganic membranes for carbon dioxide separation has also received increasing attention. However, few adsorbents or membranes reported so far have desired properties for high temperature CO₂ separation. In this study, we focused on lithium zirconate as a potential material for making dense ceramic membrane for carbon dioxide separation.

In the 1st half year, we prepared pure lithium zirconate by solid state reaction method and examined the influence of the preparation conditions such as calcination temperatures on CO₂ sorption properties. Phase structure analysis using XRD shows that the obtained lithium zirconate is in a defect sodium chloride structure (monoclinic phase). Then, the CO₂ sorption properties of the obtained pure lithium zirconate were examined by TGA. The results show that this material can take a large amount of CO₂ (up to 20wt% = 4.5mmol/g) at the desired temperature range (400-600 °C). Compared to the other CO₂ sorption materials such as physical sorbents, lithium zirconate not only offers highest sorption capacity, but also is the only sorbent that can be operated at high temperatures. Furthermore, compared to most physical sorbents which have limited CO₂/N₂ selectivity, the lithium zirconate does not adsorb nitrogen at all. This means that lithium zirconate would give an infinitely large CO₂/N₂ selectivity. In the pure Li₂ZrO₃, however, sorption rate is very slow in spite of large CO₂ sorption capacity. Doping of K₂CO₃/Li₂CO₃ in Li₂ZrO₃ (this is referred to modified Li₂ZrO₃) improved CO₂ sorption rate considerably. In the modified case, CO₂ sorption rate is 40 times faster than the pure case.

In the 2nd half research, we conducted various kinds of experiments to understand the CO₂ sorption/desorption mechanism on the pure and modified Li₂ZrO₃ with the help of TGA, DSC-TGA and XRD. First, we examined the effect of the operational temperatures and the CO₂ partial pressures on the CO₂ sorption in the case of modified lithium zirconate. The results show that compared to the CO₂ sorption at 500 °C, CO₂ sorption rate at 400 °C is very slow and almost the same as in the case of pure lithium zirconate. It was also found that CO₂ partial pressure affected the CO₂ sorption rate, that is, CO₂ sorption rate increased with the increase of the CO₂ partial pressure. The microstructure change of the modified lithium zirconate during CO₂ sorption/desorption process was studied by XRD. The results clearly show that the reaction between lithium zirconate and CO₂ is reversible during CO₂ sorption/desorption process. DSC-TGA analysis for CO₂ sorption/desorption process was also carried out both in the case of pure and modified lithium zirconate. The obtained results suggest that the melting of Li/K carbonate mixture may play an important role in rapid CO₂ sorption in the case of modified lithium zirconate. Finally, we carried out the experiments on the CO₂ desorption process from both the pure and modified lithium zirconates. The results indicate little difference for CO₂ desorption process between the pure and modified lithium zirconates.

EXPERIMENTAL

Effect of Temperature and Partial Pressure of CO₂ on CO₂ Sorption Properties

To examine the effect of temperature on CO₂ sorption properties of lithium zirconate, CO₂ sorption experiment was carried out at 400 °C by TGA. The modified lithium zirconate prepared from Li₂CO₃ + ZrO₂ + K₂CO₃ (1.1 : 1.0 : 0.2) at 850 °C was used in this experiment. Also, the effect of CO₂ partial pressure on CO₂ sorption properties was examined by changing CO₂ partial pressure from 0.2 to 1atm at 400 °C.

Analysis of Phase Structure Change during CO₂ Sorption/Desorption Process

To analyze the structure change of modified lithium zirconate during the CO₂ sorption/desorption process, modified lithium zirconates were rapidly quenched to the room temperature after CO₂ sorption at 500 °C and after CO₂ desorption at 780 °C, respectively. Then, the quenched samples were analyzed by XRD.

DSC-TGA Analysis

To examine the effect of Li/K carbonate in the case of modified lithium zirconate on the CO₂ sorption property, differential scanning calorimetry-thermogravimetric analysis (DSC-TGA; TA Instrument, SDT 2960) was carried out for both pure and modified lithium zirconates under the flow of CO₂ (flow rate: 100ml/min). The pure and modified lithium zirconate used in this study were prepared from Li₂CO₃ + ZrO₂ (1.0 : 1.0) at 850 °C and from Li₂CO₃ + ZrO₂ + K₂CO₃ (1.1 : 1.0 : 0.2) at 850 °C, respectively. The following temperature program was used in the DSC-TGA experiment;

1. Equilibrate at 50 °C
2. Ramp 10 °C/min to 110 °C
3. Isothermal for 30 min
4. Ramp 10 °C/min to 1000 °C

Examination of CO₂ Desorption Properties of Pure and Modified Li₂ZrO₃

CO₂ desorption properties of the pure lithium zirconate were studied by TGA in a microelectronic recording balance system (CAHN C-1000), and compared with the result in the case of modified lithium zirconate. 152mg of pure lithium zirconate powders prepared at 850 °C were placed in the sample pan. The sample was first dried by passing dry air for 30 min at 500 °C and then CO₂ sorption was carried out by changing the purge gas from dry air to CO₂. After 17 wt % CO₂ sorption, temperature was changed to 780 °C to proceed CO₂ desorption reaction. At the last stage, purge gas was changed from CO₂ to dry air at 780 °C to increase CO₂ desorption rate. The gas flow rate was maintained at 200 ml/min by mass flow controllers.

RESULTS AND DISCUSSION

Effect of Temperature and Partial Pressure of CO₂ on CO₂ Sorption Properties

Figure 1 shows the CO₂ sorption uptake curves at 400 °C in various CO₂ partial pressures for the modified lithium zirconate. Compared to the CO₂ sorption at 500 °C, CO₂ sorption rate at 400 °C is very slow and almost the same as in the case of pure lithium zirconate. At this temperature, produced lithium carbonate from CO₂ sorption reaction and Li/K carbonate mixture contained originally in modified lithium zirconate should be in solid state since their melting points are 723 °C and 498 °C, respectively. It was also found that CO₂ partial pressure affected the CO₂ sorption rate, that is, CO₂ sorption rate increased with the increase of CO₂ partial pressure. This seems to suggest that under this condition, the rate-limiting process is diffusion of CO₂ in the solid state Li/K carbonate mixture. However, equilibrium amount of CO₂ uptake was not affected by the CO₂ partial pressure.

Microstructure Change of Lithium Zirconate during CO₂ Sorption/Desorption Process

The microstructure change of the modified lithium zirconate during CO₂ sorption/desorption process was studied by XRD. Figures 2-(b), (c) shows the XRD patterns of the quenched samples of the modified lithium zirconate after CO₂ sorption and desorption. XRD pattern of the modified lithium zirconate before CO₂ sorption (original state) is given in Fig.2-(a). Compared to Fig.2-(a), the XRD pattern in Fig.2-(b) shows that the peaks of lithium zirconate monoclinic structure completely disappear and zirconium oxide peaks are presented instead. This result indicates that after CO₂ sorption process, lithium zirconate reacted almost completely with CO₂ to become zirconium oxide and lithium carbonate. However, the peaks of lithium carbonate was undetectable. The XRD pattern in Fig.2-(c) includes the peaks of only lithium zirconate monoclinic structure without other peaks. This means that after CO₂ desorption process at 780 °C, lithium carbonate and zirconium oxide react again and return to lithium zirconate with monoclinic structure by releasing of CO₂. These results confirm that the reaction between lithium zirconate and CO₂ is reversible during CO₂ sorption/desorption process.

Results of DSC-TGA Analysis

Figure 3-(a), (b) show the results of DSC-TGA analysis for pure and modified lithium zirconate under CO₂ atmosphere, respectively. In the case of pure lithium zirconate, a broad exothermic peak is observed between 450 and 650 °C. This peak is considered from the reaction between lithium zirconate and CO₂, because the reaction is exothermic. At the same time, weight increase occurs. The sharp endothermic peak around 720 °C may include both melting of produced lithium carbonate and a CO₂ desorption reaction, since this sharp peak is at the same temperature as the melting point of lithium carbonate (723 °C) and the CO₂ desorption process, indicated by the weight decrease, is endothermic. This result indicates that in the case of pure lithium zirconate, produced lithium carbonate is in solid state after CO₂ sorption reaction.

Different from the pure lithium zirconate case, there is a sharp endothermic peak at around

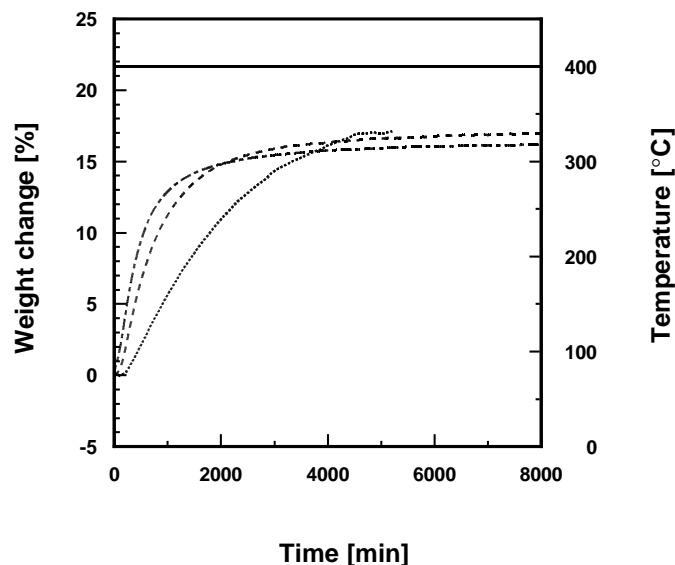
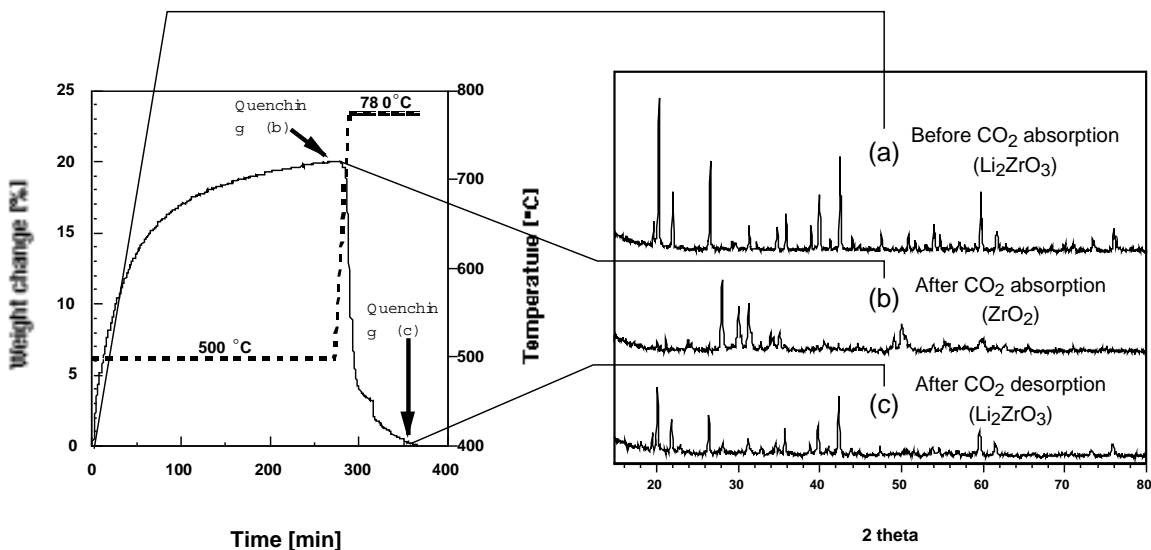


Fig.1 Effect of temperature and CO₂ partial pressure on the CO₂ sorption rate in the case of modified lithium zirconate

Gas : CO₂ 20 - 50 %, balanced by nitrogen, atmospheric pressure.

Initial sample weight : --- mg, Gas flow rate : 100 ml/min.



Figs.2 (a) - (c) Changes of XRD patterns of the Li₂ZrO₃ by CO₂ sorption and desorption

500 °C for the modified case. This endothermic peak agrees well with the rapid increase of the sample weight. It is known that the mixture of lithium and potassium carbonates can form an eutectic mixture. Although the melting points of pure Li and K carbonate are 723 and 891 °C, respectively, the melting point of their mixture is lower, with a minimum at 498 °C. This temperature agrees with the endothermic peak at around 500 °C. Therefore, the peak is considered from the melting of Li/K eutectic mixture. Figure 4 shows the phase diagram of the binary system of Li/K carbonate [5]. This peak is the only difference between the pure and modified lithium zirconate cases during CO₂ sorption process. This difference is responsible for rapid CO₂ sorption on the modified lithium zirconate.

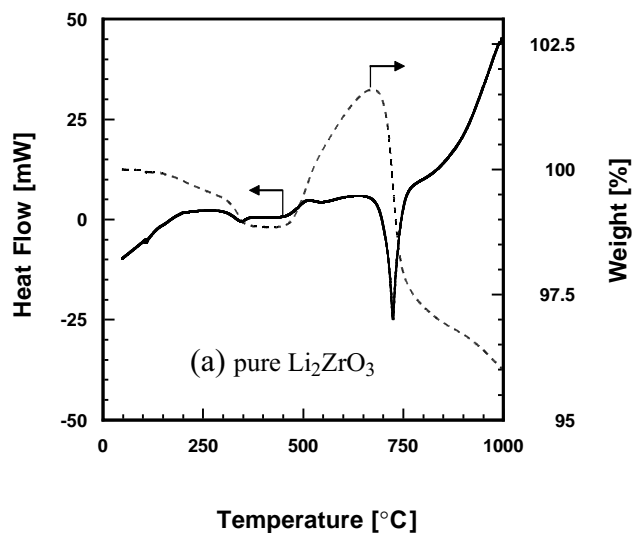
For the modified lithium zirconate case, a slightly broad exothermic peak is also observed at around 800 °C. Similar to the pure lithium, the weight decrease of the sample occurs at the same time. Therefore, this peak is also considered from CO₂ desorption.

CO₂ Desorption Properties of Pure and Modified Lithium Zirconate

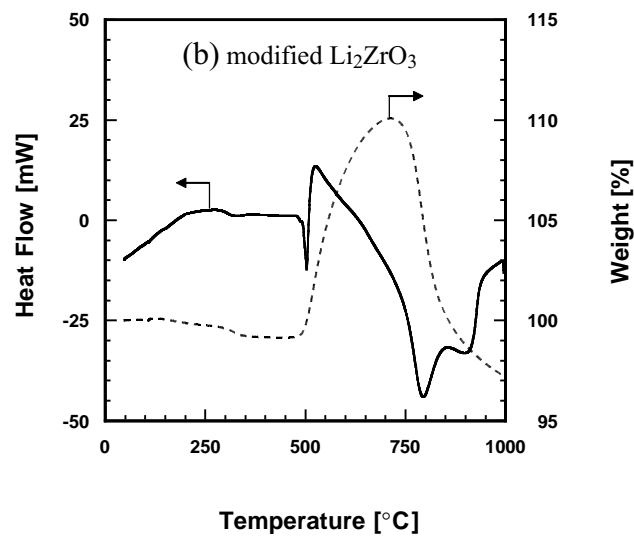
Figure 5 shows the comparison of CO₂ desorption process in the case of pure and modified lithium zirconate. In both cases, about 80 % of absorbed CO₂ is desorbed from the sample within 80 min and 50 min, respectively, after the temperature is raised to 780 °C in the same CO₂ containing surrounding gas as CO₂ sorption process. The remaining adsorbed CO₂ can be completely desorbed after the surrounding gas is switched to pure dry air. In contrast to the CO₂ sorption process, CO₂ desorption rates in both cases are similar. A small difference could come from the difference in surrounding gas during the CO₂ desorption process. The operational temperature is the same for both pure and modified lithium zirconate cases (780 °C) in the desorption process. However, CO₂ concentration in the surrounding gas for the pure case (100% CO₂) is much higher than that for the modified case (50 %CO₂) at the beginning of the desorption process. This may result in a slightly faster CO₂ desorption rate for the modified lithium zirconate. The results obtained in this experiment indicate that there is little difference for CO₂ desorption process between pure and modified lithium zirconate cases.

CONCLUSION

In the past half year, we conducted various kinds of experiments to understand the CO₂ sorption/desorption mechanism on the pure and modified lithium zirconate with the help of TGA, DSC-TGA and XRD. First, we examined the effect of the operational temperatures and the CO₂ partial pressures on the CO₂ sorption on modified lithium zirconate. Compared to the CO₂ sorption at 500 °C, the rate of CO₂ sorption on modified lithium zirconate at 400 °C is very slow and almost the same as in the case of pure lithium zirconate. CO₂ sorption rate increases with the increase of the CO₂ partial pressure. The microstructure change of the modified lithium zirconate during CO₂ sorption/desorption process was studied by XRD. The results clearly show that the reaction between lithium zirconate and CO₂ is reversible during CO₂ sorption/desorption process. DSC-TGA analysis for CO₂ sorption/desorption process was also carried out for both pure and modified lithium zirconates. The obtained results suggest that the melting of Li/K carbonates mixture may play an important role in rapid CO₂ sorption in the case of modified lithium zirconate. Finally, we carried



Starting materials
 Li_2CO_3 : ZrO_2
 = 1.0 : 1.0
 Calcined at 850°C 12h



Starting materials
 Li_2CO_3 : ZrO_2 : K_2CO_3
 = 1.1 : 1.0 : 0.2
 Calcined at 850°C 12h

Figs.3 DSC-TGA results (under CO_2 purge gas)

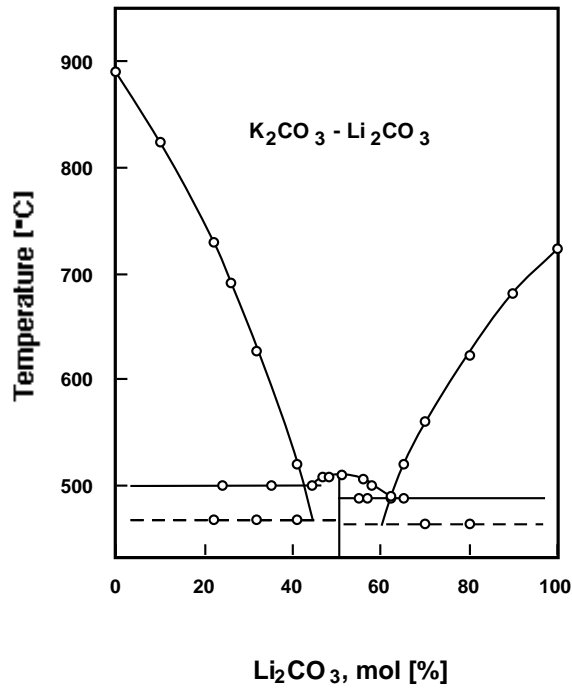


Fig.4 Phese diagram of Li/K carbonate

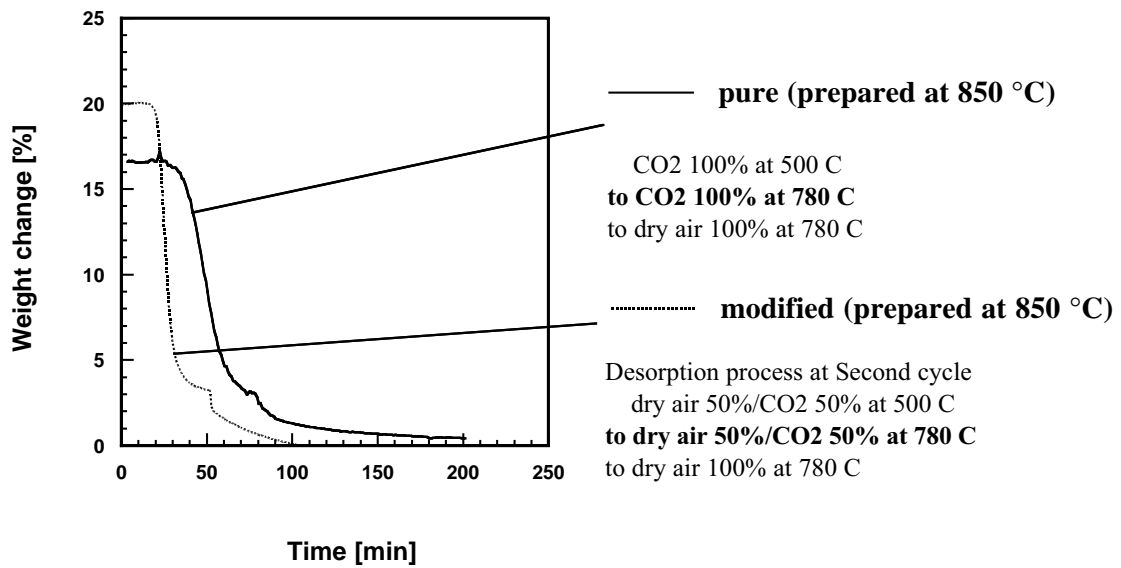


Fig.5 Comparison of CO₂ desorption process in the case of pure and modified lithium zirconate.

out the experiment on the CO₂ desorption for both pure and modified lithium zirconates. The results indicate that there is little difference for CO₂ desorption process between pure and modified lithium zirconate case. We are currently studying more detailed mechanisms of CO₂ sorption and desorption on the pure and modified lithium zirconates.

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