Novel Ceramic Membrane for High Temperature Carbon Dioxide Separation

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Jerry Y. S. Lin
Jun-ichi Ida

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University of Cincinnati
Department of Chemical Engineering
Mail Location 171
Cincinnati, OH 45221-0171

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ABSTRACT

This project is aimed at demonstrating technical feasibility for a lithium zirconate based dense ceramic membrane for separation of carbon dioxide from flue gas at high temperature. The research work conducted in this reporting period was focused on several fundamental issues of lithium zirconate important to the development of the dense inorganic membrane. These fundamental issues include material synthesis of lithium zirconate, phases and microstructure of lithium zirconate and structure change of lithium zirconate during sorption/desorption process. The results show difficulty to prepare the dense ceramic membrane from pure lithium zirconate, but indicate a possibility to prepare the dense inorganic membrane for carbone dioxide separation from a composite lithium zirconate.

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INTRODUCTION

Flue gas from coal-burning plants is the major source point for generation of carbon dioxide in the atmosphere. Before carbon dioxide can be sequestered from flue gas it must be captured as a relatively pure gas. Separation of carbon dioxide from flue gas presents several technical challenges. First, the two major constituents in flue gas (carbon dioxide and nitrogen) are very similar in molecular sizes. It is difficult to identify a separation medium based on the most common size sieving separation principle for separation of these two molecules. Second, flue gas from coal-burners is warm and it is highly desired to separate carbon dioxide from flue gas at a high temperature (above 400 °C) without cooling the flue gas to room or even lower temperature. However, the existing separation technologies are not able to separate carbon dioxide over other gases in the high temperatures. Third, the volume of carbon dioxide in the flue gas is extremely large, in terms of both volumetric flow rate of flue gas and the concentration of carbon dioxide. Many existing technologies suitable for separation of carbon dioxide from industrial streams become cost ineffective for separation of carbon dioxide from flue gas.

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 carbone dioxide separation. We examined several fundamental issues related to the development of the lithium zirconate membrane for separation of carbon dioxide from flue gas. These fundamental issues include material synthesis of lithium zirconate, phases and microstructure of lithium zirconate, structure change of the material during sorption/desorption process.

EXECTIVE SUMMARY

Flue gas from coal-burning plants is the major source point for generation of carbon dioxide in the atmosphere. Separation of carbon dioxide from flue gas presents several technical challenges. Many existing technologies suitable for separation of carbon dioxide from industrial streams become cost ineffective for separation of carbon dioxide from flue gas. 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 synthesize a non-porous, dense ceramic membrane for separation of carbon dioxide from flue gas at high temperatures.

In this study, we focus on lithium zirconate as a potential material for making the dense ceramic membranes for carbon dioxide separation. We are investigating several fundamental issues including material synthesis of lithium zirconate, phases and microstructure of lithium zirconate, structure change of the material during sorption/desorption process, and mechanism of the carbon dioxide sorption in lithium zirconate. Understanding of these fundamental issues is critical to the design and development of the dense membrane for carbon dioxide separation.

Lithium zirconate powders were prepared from lithium carbonate and zirconium oxide (1:1) by a solid state method at various calcination temperatures. XRD analysis shows that the monoclinic lithium zirconate could be prepared in the calcination temperature range from 850 to 1200 °C. At lower temperatures the solid state reactions could not be completed, and higher calcination temperatures resulted in formation of zirconia due to evaporation of lithium containing species.

Carbon dioxide sorption/desorption properties of the obtained lithium zirconate was examined. Carbon dioxide sorption was hardly observed in the case with pure lithium zirconate powder, due to slow sorption kinetic. However, addition of potassium carbonate and lithium carbonate in the lithium zirconate remarkably improved carbon dioxide sorption properties of the lithium zirconate material. In this case, clear weight increase and decrease of the sample were observed during carbon dioxide sorption/desorption process. The value of the weight increases is 20 % after 270 min carbon dioxide sorption, corresponding to 85 % of the theoretical maximum. The sorption and desorption processes completed within 300 minutes.

The microstructure of the lithium zirconate ceramics before and after sorption of carbon dioxide was studied with the help of TGA, DSC and XRD in order to understand the mechanism of carbon dioxide sorption in the material. As-prepared lithium zirconate has a defect sodium chloride structure (monoclinic phase). After sorption of carbon dioxide, a monoclinic zirconia phase is observed, with lithium carbonate (in potantisum carbonate) possibly in the liquid state. The material returns to lithium zirconate in the sodium chloride structure after regeneration. The K_2CO_3 doped lithium carbonate may have a composite microstructure with molten L_2CO_3/K_2CO_3 forming a network running through the lithium zirconate particle.

EXPERIMENTAL

Synthesis and Characterization of Li_2ZrO_3

Li_2ZrO_3 was prepared by the solid state method. Starting materials were reagent grade Li_2CO_3 and ZrO_2 (1:1) according to the report by Nakagawa and Ohashi[1]. The materials were weighed, ground, and intimately mixed in an agate mortar with a suitable amount of acetone or ethanol. The mixtures were calcined at various temperatures (500, 700, 850, 1000, 1200 and 1400 °C) for 12h. The crystalline structure of all the prepared samples was characterized by X-ray Diffraction (XRD).

CO_2 Sorption on Pure Li_2ZrO_3

CO_2 sorption properties of the obtained Li_2ZrO_3 were tested by Thermogravimetric Analysis (TGA) in a microelectronic recording balance system (CAHN C-1000). 151mg of Li_2ZrO_3 particles prepared at 1000 °C were placed in the sample pan. The sample was first dried by passing dry air for 30 min at 500 °C and then CO_2 sorption was carried out by changing the purge gas from dry air to CO_2. The gas flow rate was maintained at 200 ml/min by mass flow controllers and the temperature was kept at 500 °C by a furnace.

Modified Li_2ZrO_3

Li_2ZrO_3 was modified by addition of K_2CO_3 and Li_2CO_3 to the starting material in the preparation process. In this experiment, the preparation method used was almost the same as mentioned above, however, calcination temperature was fixed at 850 °C and various compositions of starting materials were used. The compositions in moler ratio of the starting materials studied are as follows:

$Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.1 : 1.0 : 0.2)
$Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.1 : 1.0 : 0.1)
$Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.2 : 1.0 : 0.1)
$Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.3 : 1.0 : 0)
$Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.0 : 1.0 : 0.3)

XRD analysis was carried out for all of the obtained samples. Then, by using the sample prepared from $Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.1 : 1.0 : 0.2) at 850 °C, CO_2 sorption/desorption experiment was carried out by TGA. 154 mg of sample powders were placed in the sample pan. The sample was first dried by passing dry air for 1 hour at 780 °C and then CO_2 sorption was carried out by changing the purge gas from 100 % dry air to dry air containing 50% CO_2. The gas flow rate was maintained at 150 ml/min by mass flow controllers and the temperature was kept at 500 °C in the CO_2 sorption period and then at 780 °C in the CO_2 desorption period by a furnace.

Analysis of Phase Structure Change during CO_2 Sorption/desorption Process

To analyze the structure change of Li_2ZrO_3 during the CO_2 sorption/desorption process, Li_2ZrO_3 samples were rapidly quenched to the room temperature after CO_2 sorption at 500 °C and after CO_2 desorption at 780 °C, respectively. Then, the quenched samples were analyzed by XRD.

DSC-TGA analysis

To examine the effect of Li_2CO_3 and K_2CO_3 on the CO_2 sorption property of Li_2ZrO_3, differential scanning calorymetry-thermogravimetric analysis (DSC-TGA; TA Instrument, SDT 2960) was carried out for the samples prepared from Li_2CO_3 + ZrO_2 + K_2CO_3 (1.1 : 1.0 : 0.2) at 850 °C and also for pure Li_2ZrO_3 for comparison.

RESULTS AND DISCUSSION

Synthesis and Characterization of Li_2ZrO_3

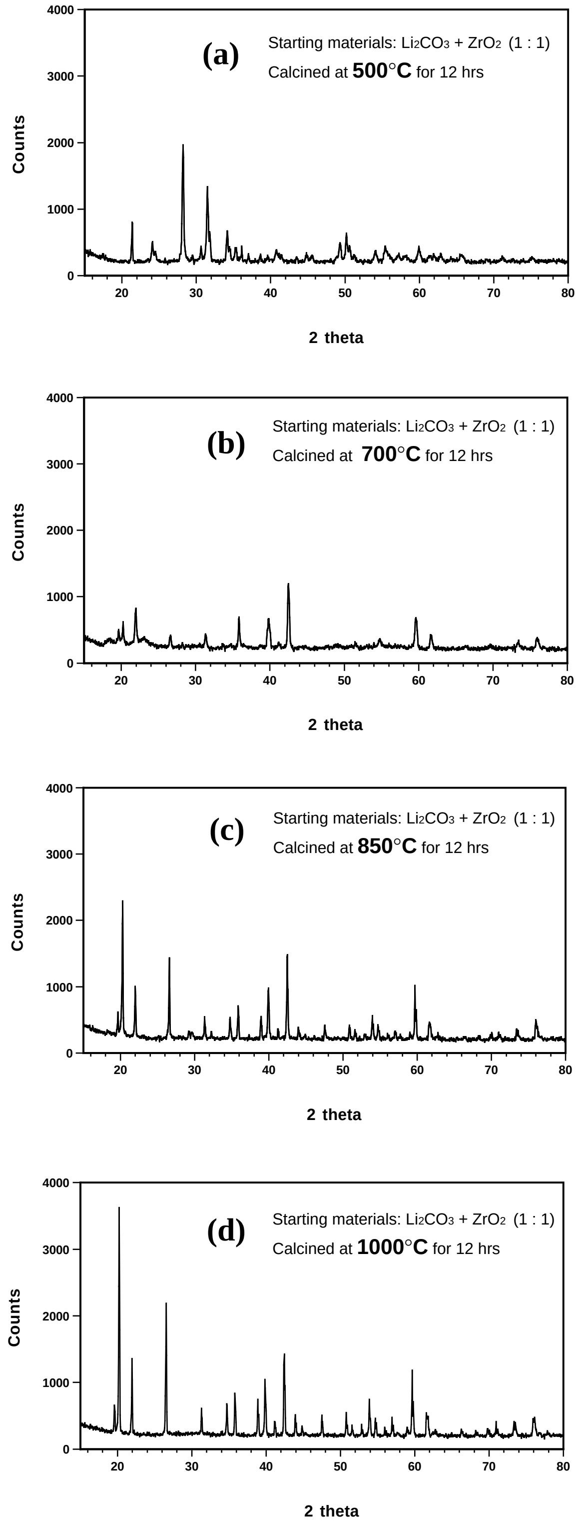
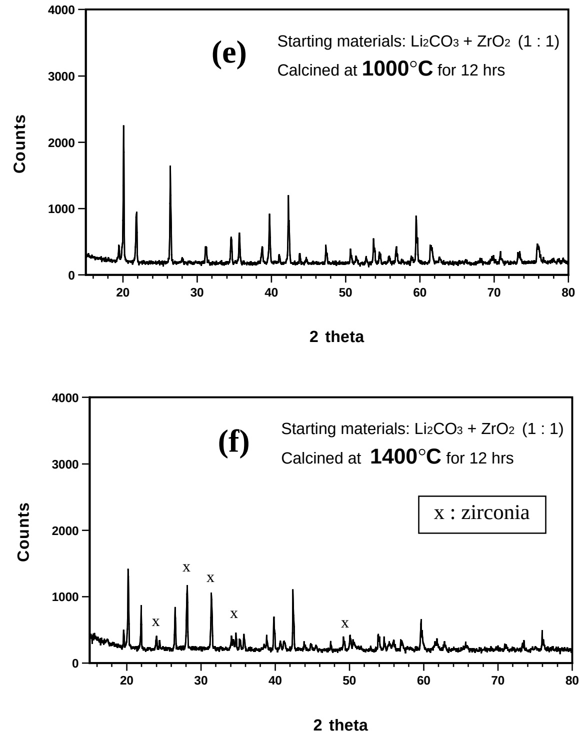
Results of the XRD analysis of the obtained samples are shown in Figs.1 (a)-(f). The XRD pattern in Fig.1-(a) clearly include the peaks of Li_2CO_3 and ZrO_2 but not the peaks of Li_2ZrO_3. This indicates that Reaction (1) does not proceed and Li_2ZrO_3 is not formed at 500 °C.

$$Li_2CO_3 + ZrO_2 = Li_2ZrO_3 + CO_2 \quad (1)$$

Some XRD peaks characteristic of Li_2ZrO_3 are observed for the sample calcined at 700 °C, as shown in Fig.1-(b). This indicates that the monoclinic Li_2ZrO_3 has already started to form at calcination temperature of 700 °C. However, the solid state reaction does not seem to have completed yet at 700 °C. In the temperature range from 850 to 1200 °C, only Li_2ZrO_3 monoclinic peaks can be seen. However, at 1400 °C, the peaks of ZrO_2 appear again in addition to the peaks of monoclinic Li_2ZrO_3. Quintana et al. [2] reported that volatilization of Li_2O from Li_2ZrO_3 occurs at 1400 °C and ZrO_2 apprears. This maybe the reason for appearance of ZrO_2. These results indicate that monoclinic Li_2ZrO_3 can be prepared in the calcination temperature range from 850 °C to 1200 °C.

CO_2 Sorption on Pure Li_2ZrO_3 by TGA

Figure 2 shows the result of the CO_2 sorption experiment on pure Li_2ZrO_3 prepared at 1000 °C. The figure shows a slow but clear increase in the sample weight. It is considered that this weight increase corresponds to CO_2 sorption on Li_2ZrO_3 based on the reverse reaction of (1) (Li_2ZrO_3 + CO_2 = Li_2CO_3 + ZrO_2). Also, it was found that it took about 7500 min to reach 20 % weight increase, and the weight was still increasing after 10000 min.

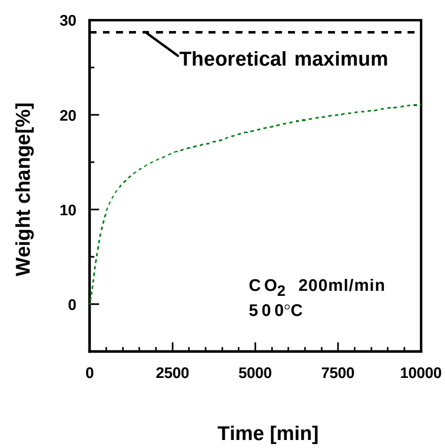


Fig.2 CO_2 absorption on pure Li_2ZrO_3 prepared at 1000°C

Figs.1 XRD pettern of Li_2ZrO_3 prepared at various temperature

Li_2ZrO_3 with Addition of K_2CO_3 and Li_2CO_3

Results of the XRD analysis of the samples prepared from starting materials of different compositions (with excess Li_2CO_3 and K_2CO_3) are given in Figs.3 (a)-(e). Figs.3-(a), (b), (e) show clearly the presence of the peaks of pure monoclinic Li_2ZrO_3. However, in Fig.3-(c), the small peaks of Li_4ZrO_4 also can be seen together with Li_2ZrO_3. Moreover, in Fig.3-(d), only peaks of Li_4ZrO_4 can be found. These results suggest that when the amount of excess Li_2CO_3 (to ZrO_2) is larger than that of K_2CO_3, Reaction (2) starts to occur instead of Reaction (1):

$2Li_2CO_3 + ZrO_2 = Li_4rO_4 + 2CO_2$ (2)

On the other hand, when the amount of K_2CO_3 is larger than that of excess Li_2CO_3, the presence of K_2CO_3 does not seem to have an influence on Li_2ZrO_3 formation reaction. In this case only Reaction (1) takes place under this experimental condition.

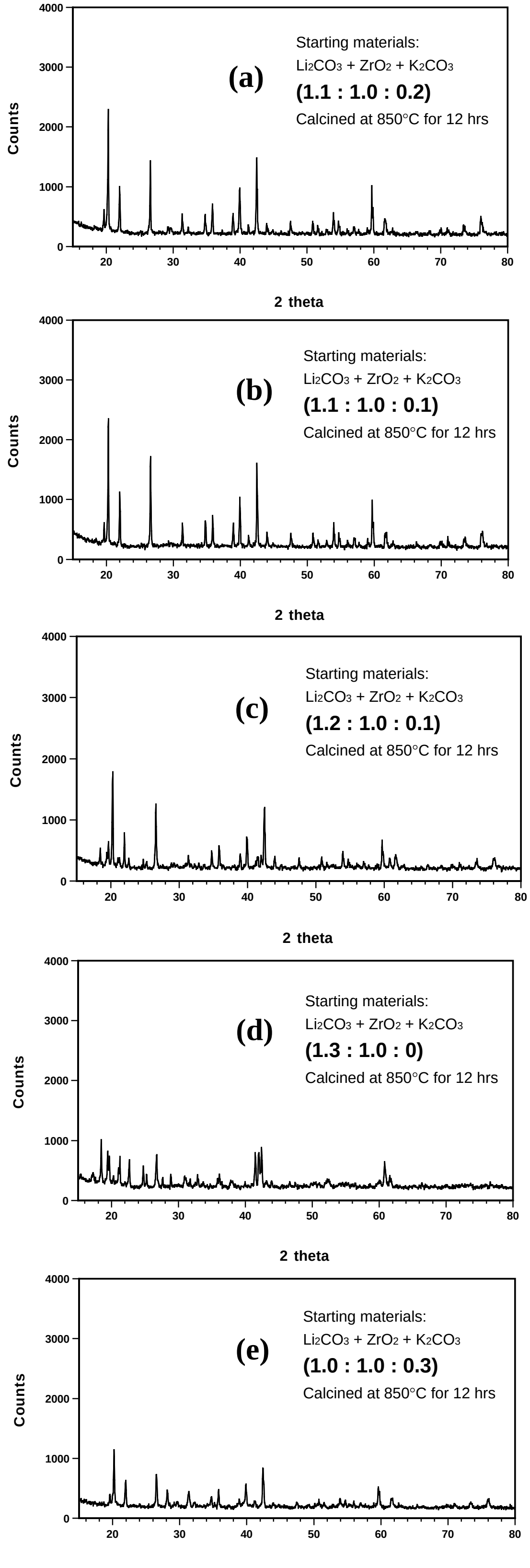
Figure 4 shows the results of the CO_2 sorption/desorption experiments on the sample prepared from $Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.1 : 1.0 : 0.2) at 850 °C. From the figure, clear weight increase and decrease are observed during CO_2 sorption (500 °C)/desorption (780 °C) process. The value of the weight increase was 20 % after 270 min CO_2 sorption, which corresponds to 85 % of the theoretical maximum. After CO_2 desorption, the weight of sample returned to the original before CO_2 sorption and similar weight change repeated in the second CO_2 sorption/desorption step. These experimental results indicate that Reaction (1) is reversible.

Phase Structure Change during CO_2 Sorption/desorption Process by XRD

Figures 5-(a), (b) shows the XRD pattern of the quenched samples of the Li_2ZrO_3 after CO_2 sorption and after CO_2 desorption, respectively. XRD pattern of the Li_2ZrO_3 before CO_2 sorption is given in Fig.3-(a). Comparing to Fig.3-(a), the XRD pattern in Fig.5-(a) shows that the peaks of Li_2ZrO_3 monoclinic structure completely disappeared and ZrO_2 peaks are present instead. This result indicates that after CO_2 sorption process, Li_2ZrO_3 reacted almost completely with CO_2 to become Li_2CO_3 and ZrO_2. The XRD pattern in Fig.5-(b) includes the peaks of only Li_2ZrO_3 monoclinic structure without other peaks. This means that after CO_2 desorption process at 780 °C, Li_2CO_3 and ZrO_2 return to Li_2ZrO_3 of monoclinic structure again. These results confirm that the reaction between Li_2ZrO_3 and CO_2 is reversible during CO_2 sorption/desorption process.

DSC-TGA Analysis

Figure 6-(a) shows the results of DSC-TGA analysis in the case with the sample prepared from $Li_2CO_3 + ZrO_2 + K_2CO_3$ (1.1 : 1.0 : 0.2) at 850 °C. Also, Fig. 6-(b) shows the results of DSC-TGA analysis in the case with pure Li_2ZrO_3 prepared at 850 °C. In Fig.6-(a), it can be seen that there is an endothermic peak at 500 °C and exothermic peak over 1200 °C. Because no peak can be seen in this temperature range for pure Li_2ZrO_3 as shown in Fig.6-(b), the endothermic peak observed in



Figs.3 XRD pettern of Li_2ZrO_3 prepared from various ratio of starting materials.

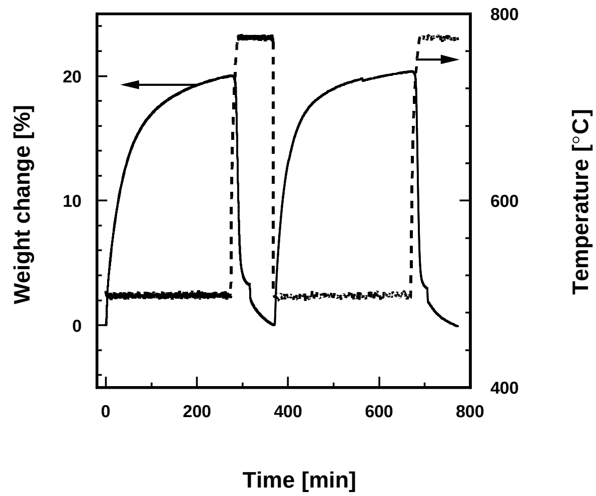
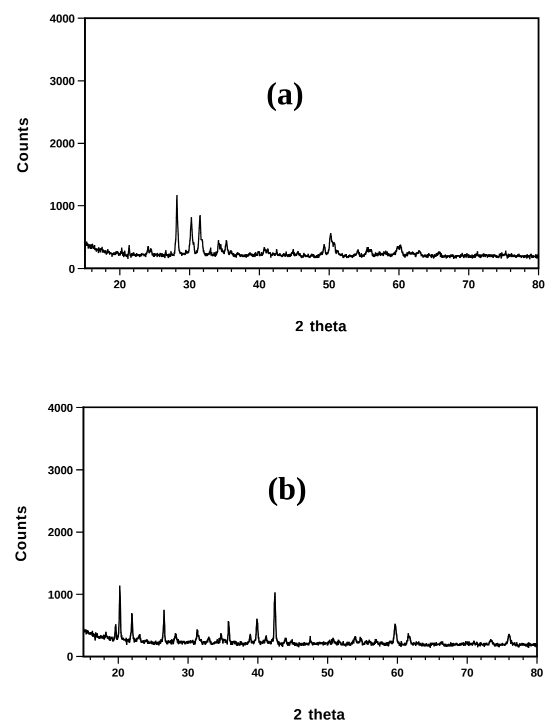
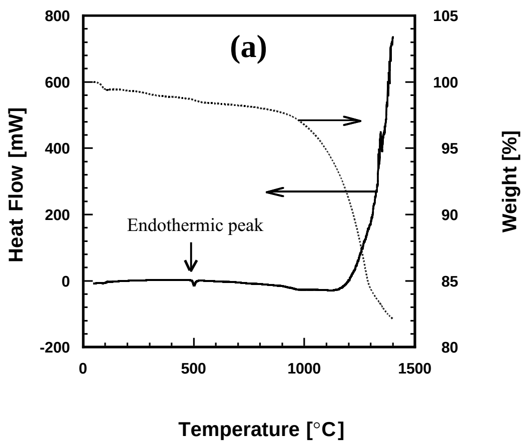


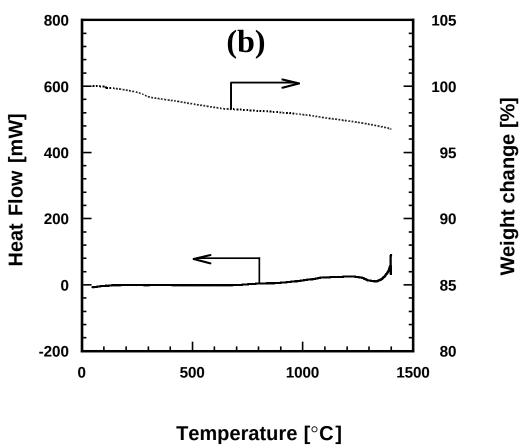
Fig.4 Weight changes of Li_2ZrO_3 powders during heating at two temperatures.
Gas : CO_2 50%, balanced by dry air, atmospheric pressure.
Initial sample weight :154 mg, Gas flow rate : 150 ml/min.



Figs.5 (a) - (b) Changes of XRD petterns of the Li_2ZrO_3 by CO_2 absorption and desorption



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



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

Figs.6 DSC-TGA results

Fig.6-(a) must be associated with Li_2CO_3 and K_2CO_3. The peak at 500 °C agrees with eutectic temperature of Li_2CO_3/K_2CO_3 mixture [3]. It is highly possible that during the heating process the solid mixture of Li_2CO_3 and K_2CO_3 in the Li_2ZrO_3 particle melts and becomes molten carbonate at 500 °C. The final Li_2ZrO_3 particle contains a Li_2ZrO_3 phase with a continuous network of Li_2CO_3 and K_2CO_3 mixture which melts at the sorption temperature.

With such microstructure, it is easier to explain the different CO_2 sorption rates observed on pure Li_2ZrO_3 and modified Li_2ZrO_3. In the former case, sorption of CO_2 on the external surface of the particle results in a formation of a dense ZrO_2 layer, which inhibits further reaction of CO_2 with the unreacted Li_2ZrO_3. In the modified Li_2ZrO_3, CO_2 can migrate into the inside of Li_2ZrO_3 particle by passing through a network of the molten carbonate of Li_2CO_3 and K_2CO_3, resulting in a faster CO_2 sorption rate.

The peak over 1200 °C in the DSC-TGA data shown in Figure 6 is considered from decompositon of Li_2CO_3/K_2CO_3 mixture, because there is a large weight loss almost in the same temperature range and this weight loss corresponds to the weight percentage of Li_2CO_3/K_2CO_3 mixture in the sample.

CONCLUSION

Several fundamental issues related to the development of lithium zirconate membrane for separation of carbon dioxide from flue gas were examined. Experimental procedure for preparing lithium zirconate powder was established. Lithium zirconate with desired phase could be prepared in the calcination temperature range from 850 to 1200 °C. Both pure Li_2ZrO_3 and Li_2ZrO_3 doped with K_2CO_3 and Li_2CO_3 can take up to 20 wt% of CO_2. However, the CO_2 sorption rate in pure Li_2ZrO_3 is too slow due possibly to the formation of zirconia covering the particle surface. This suggests that it is unlikely that one can prepare practically useful dense membrane from pure Li_2ZrO_3 for CO_2 separation. However, the K_2CO_3 and Li_2CO_3 doped Li_2ZrO_3 exhibits a much fast CO_2 sorption/desorption rate. The reaction between Li_2ZrO_3 and CO_2 is reversible during CO_2 sorption/desorption process. TGA/DSC/XRD analysis has shown a unique microstructure of the K_2CO_3 and Li_2CO_3 doped Li_2ZrO_3 particles. These results indicate that it is possible to prepare dense ceramic membrane from the modified Li_2ZrO_3 powder for high temperature CO_2 separation. More research, including sorption equilibrium and kinetics on the modified Li_2ZrO_3 (to be conducted in the second half year of this project), will provide more clear answer as to the feasibility and design of the lithium zirconate dense membrane.

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