Novel Ceramic Membrane for High Temperature Carbon Dioxide Separation

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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 carbon 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 potassium carbonate) possibly in the liquid state. The material returns to lithium zirconate in the sodium chloride structure after regeneration. The K2CO3 doped lithium carbonate may have a composite microstructure with molten L2CO3/K2CO3 forming a network running through the lithium zirconate particle.
EXPERIMENTAL

Synthesis and Characterization of Li$_2$ZrO$_3$

Li$_2$ZrO$_3$ was prepared by the solid state method. Starting materials were reagent grade Li$_2$CO$_3$ 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$_2$ZrO$_3$

CO$_2$ sorption properties of the obtained Li$_2$ZrO$_3$ were tested by Thermogravimetric Analysis (TGA) in a microelectronic recording balance system (CAHN C-1000). 151mg of Li$_2$ZrO$_3$ 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$_2$ZrO$_3$

Li$_2$ZrO$_3$ was modified by addition of K$_2$CO$_3$ and Li$_2$CO$_3$ 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 molar ratio of the starting materials studied are as follows:

- Li$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (1.1 : 1.0 : 0.2)
- Li$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (1.1 : 1.0 : 0.1)
- Li$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (1.2 : 1.0 : 0.1)
- Li$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (1.3 : 1.0 : 0)
- Li$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (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$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (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 CO2 Sorption/desorption Process

To analyze the structure change of Li2ZrO3 during the CO2 sorption/desorption process, Li2ZrO3 samples 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 Li2CO3 and K2CO3 on the CO2 sorption property of Li2ZrO3, differential scanning calorimetry-thermogravimetric analysis (DSC-TGA; TA Instrument, SDT 2960) was carried out for the samples prepared from Li2CO3 + ZrO2 + K2CO3 (1.1 : 1.0 : 0.2) at 850 °C and also for pure Li2ZrO3 for comparison.

RESULTS AND DISCUSSION

Synthesis and Characterization of Li2ZrO3

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 Li2CO3 and ZrO2 but not the peaks of Li2ZrO3. This indicates that Reaction (1) does not proceed and Li2ZrO3 is not formed at 500 °C.

Li2CO3 + ZrO2 = Li2ZrO3 + CO2 (1)

Some XRD peaks characteristic of Li2ZrO3 are observed for the sample calcined at 700 °C, as shown in Fig.1-(b). This indicates that the monoclinic Li2ZrO3 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 Li2ZrO3 monoclinic peaks can be seen. However, at 1400 °C, the peaks of ZrO2 appear again in addition to the peaks of monoclinic Li2ZrO3. Quintana et al. 2) reported that volatilization of Li2O from Li2ZrO3 occurs at 1400 °C and ZrO2 appears. This maybe the reason for appearance of ZrO2. These results indicate that monoclinic Li2ZrO3 can be prepared in the calcination temperature range from 850 °C to 1200 °C.

CO2 Sorption on Pure Li2ZrO3 by TGA

Figure 2 shows the result of the CO2 sorption experiment on pure Li2ZrO3 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 CO2 sorption on Li2ZrO3 based on the reverse reaction of (1) (Li2ZrO3 + CO2 = Li2CO3 + ZrO2). Also, it was found that it took about 7500 min to reach 20 % weight increase, and the weight was still increasing after 10000 min.
Starting materials: Li$_2$CO$_3$ + ZrO$_2$ (1 : 1)
Calcined at 500°C for 12 hrs

Starting materials: Li$_2$CO$_3$ + ZrO$_2$ (1 : 1)
Calcined at 700°C for 12 hrs

Starting materials: Li$_2$CO$_3$ + ZrO$_2$ (1 : 1)
Calcined at 850°C for 12 hrs

Starting materials: Li$_2$CO$_3$ + ZrO$_2$ (1 : 1)
Calcined at 1000°C for 12 hrs

Starting materials: Li$_2$CO$_3$ + ZrO$_2$ (1 : 1)
Calcined at 1400°C for 12 hrs

Fig.2 CO$_2$ absorption on pure Li$_2$ZrO$_3$ prepared at 1000°C

Figs.1 XRD pattern of Li$_2$ZrO$_3$ prepared at various temperature
Li$_2$ZrO$_3$ with Addition of K$_2$CO$_3$ and Li$_2$CO$_3$

Results of the XRD analysis of the samples prepared from starting materials of different compositions (with excess Li$_2$CO$_3$ and K$_2$CO$_3$) are given in Figs.3 (a)-(e). Figs.3-(a), (b), (e) show clearly the presence of the peaks of pure monoclinic Li$_2$ZrO$_3$. However, in Fig.3-(c), the small peaks of Li$_4$ZrO$_4$ also can be seen together with Li$_2$ZrO$_3$. Moreover, in Fig.3-(d), only peaks of Li$_4$ZrO$_4$ can be found. These results suggest that when the amount of excess Li$_2$CO$_3$ (to ZrO$_2$) is larger than that of K$_2$CO$_3$, Reaction (2) starts to occur instead of Reaction (1):

$$2\text{Li}_2\text{CO}_3 + \text{ZrO}_2 = \text{Li}_4\text{rO}_4 + 2\text{CO}_2 \ (2)$$

On the other hand, when the amount of K$_2$CO$_3$ is larger than that of excess Li$_2$CO$_3$, the presence of K$_2$CO$_3$ does not seem to have an influence on Li$_2$ZrO$_3$ 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$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (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$_2$ZrO$_3$ after CO$_2$ sorption and after CO$_2$ desorption, respectively. XRD pattern of the Li$_2$ZrO$_3$ 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$_2$ZrO$_3$ monoclinic structure completely disappeared and ZrO$_2$ peaks are present instead. This result indicates that after CO$_2$ sorption process, Li$_2$ZrO$_3$ reacted almost completely with CO$_2$ to become Li$_2$CO$_3$ and ZrO$_2$. The XRD pattern in Fig.5-(b) includes the peaks of only Li$_2$ZrO$_3$ monoclinic structure without other peaks. This means that after CO$_2$ desorption process at 780 °C, Li$_2$CO$_3$ and ZrO$_2$ return to Li$_2$ZrO$_3$ of monoclinic structure again. These results confirm that the reaction between Li$_2$ZrO$_3$ 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$_2$CO$_3$ + ZrO$_2$ + K$_2$CO$_3$ (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$_2$ZrO$_3$ 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$_2$ZrO$_3$ as shown in Fig.6-(b), the endothermic peak observed in
Figs. 3 XRD patterns of Li$_2$ZrO$_3$ prepared from various ratios of starting materials.

Figs. 4 Weight changes of Li$_2$ZrO$_3$ 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 patterns of the Li$_2$ZrO$_3$ by CO$_2$ absorption and desorption.
Figs. 6 DSC-TGA results

(a) Starting materials
Li$_2$CO$_3$ : ZrO$_2$ : K$_2$CO$_3$  
= 1.1 : 1.0 : 0.2  
Calcined at 850°C 12h

(b) Starting materials
Li$_2$CO$_3$ : ZrO$_2$  
= 1.0 : 1.0  
Calcined at 850°C 12h
Fig. 6-(a) must be associated with Li$_2$CO$_3$ and K$_2$CO$_3$. The peak at 500 °C agrees with eutectic temperature of Li$_2$CO$_3$/K$_2$CO$_3$ mixture $^3$. It is highly possible that during the heating process the solid mixture of Li$_2$CO$_3$ and K$_2$CO$_3$ in the Li$_2$ZrO$_3$ particle melts and becomes molten carbonate at 500 °C. The final Li$_2$ZrO$_3$ particle contains a Li$_2$ZrO$_3$ phase with a continuous network of Li$_2$CO$_3$ and K$_2$CO$_3$ 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$_2$ZrO$_3$ and modified Li$_2$ZrO$_3$. 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$_2$ZrO$_3$. In the modified Li$_2$ZrO$_3$, CO$_2$ can migrate into the inside of Li$_2$ZrO$_3$ particle by passing through a network of the molten carbonate of Li$_2$CO$_3$ and K$_2$CO$_3$, 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 decomposition of Li$_2$CO$_3$/K$_2$CO$_3$ 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$_2$CO$_3$/K$_2$CO$_3$ 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$_2$ZrO$_3$ and Li$_2$ZrO$_3$ doped with K$_2$CO$_3$ and Li$_2$CO$_3$ can take up to 20 wt% of CO$_2$. However, the CO$_2$ sorption rate in pure Li$_2$ZrO$_3$ 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$_2$ZrO$_3$ for CO$_2$ separation. However, the K$_2$CO$_3$ and Li$_2$CO$_3$ doped Li$_2$ZrO$_3$ exhibits a much fast CO$_2$ sorption/desorption rate. The reaction between Li$_2$ZrO$_3$ and CO$_2$ is reversible during CO$_2$ sorption/desorption process. TGA/DSC/XRD analysis has shown a unique microstructure of the K$_2$CO$_3$ and Li$_2$CO$_3$ doped Li$_2$ZrO$_3$ particles. These results indicate that it is possible to prepare dense ceramic membrane from the modified Li$_2$ZrO$_3$ powder for high temperature CO$_2$ separation. More research, including sorption equilibrium and kinetics on the modified Li$_2$ZrO$_3$ (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.

Reference