Novel Inorganic Membranes for High Temperature Carbon Dioxide Separation

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ABSTRACT

We studied feasibility of two types of dense inorganic membranes which are fundamentally different from those porous inorganic membranes reported in the literature for separation of carbon dioxide from gas streams at high temperatures. The first is a symmetric, dense membrane made of Li₂ZrO₃ and the second is a dual-phase metal-carbonate membrane. We have identified a unique CO₂ sorption/desorption mechanism on lithium zirconate. Considering the all obtained data, we proposed a double layer model to describe the CO₂ sorption/desorption behavior of lithium zirconate. In the model, final product after CO₂ sorption is a particle which consists of a ZrO₂ core inside and a Li₂CO₃ shell. The understanding of CO₂ sorption mechanisms suggests a means to improve CO₂ sorption rate on this group of oxides. It also leads to the conclusion that lithium zirconate is not a suitable material for the proposed dense ceramic membrane for CO₂ separation. Following the second concept of dense membrane for CO₂ separation, we succeeded in preparing the hermetic (gas-tight) dense inorganic membrane consisting of a porous metal phase and a molten carbonate phase. The metal phase not only provides the mechanical support but also is electronically conducting, reducing the overall mass transfer resistance for CO₂ permeation through the membrane. Permeation data showed that nitrogen or helium is not permeable through these membranes (only CO_2 , with O_2) can permeate through the membrane based on the transport mechanism). This dual-phase membrane may offer promising properties for applications in membrane processes for separation of CO₂ from flue (or coal gasification gas) at high temperatures (350-550°C).

INTRODUCTION

Efficient separation of carbon dioxide from flue gas is key to carbon dioxide sequestration and control of the greenhouse gas. In this project, we studied feasibility of two types of dense inorganic membranes which are fundamentally different from porous inorganic membranes which have been studied for CO_2 separation. The first is a symmetric, dense membrane made of Li_2ZrO_3 and the second is a dual-phase metal-carbonate membrane. They were designed for carbon dioxide separation in the temperature range of 400-600°C.

The first concept was based on a recent study conducted by Nakagawa and Ohashi of Toshiba who reported in a short communication [1] good carbon dioxide sorption properties for Li_2ZrO_3 in 500-700°C. Carbon dioxide sorption capacity is 100 mg/g at temperature of 600°C and P_{CO2} of 0.7 atm. They found that the carbonated sorbent can be regenerated to Li_2ZrO_3 by

varying the temperature, or by reducing the carbon dioxide pressure. The regenerated ceramic can be used in subsequent sorption steps. Unlike most other oxides that can react with carbon dioxide to form carbonates, the particles made of this ceramic could maintain their mechanical integrity after repeated cycles of carbonation and regeneration. Furthermore, the carbon dioxide sorption capacity of this material is not affected by the presence of water vapor and hydrogen in the gas stream.

A membrane made of Li_2ZrO_3 , as shown in Figure 1, could be permeable only to carbon dioxide since Li_2ZrO_3 only takes carbon dioxide. Li_2ZrO_3 meets the following three requirements as the dense



Figure 1 First Concept of Dense Inorganic Membrane Based on Li₂ZrO₃ for High Temperature Carbon Dioxide Separation

membrane material: (1) The material can absorb a considerable amount of carbon dioxide in the bulk of the material in the specified temperature range; (2) The sorption is a reversible, i.e., the sorbed carbon dioxide can be easily desorbed; (3) Sorption of other gases (such as hydrogen) is negligible and the presence of these gases does not affect the sorption of carbon dioxide.

The membrane materials, however, should also meet the other three requirements: (4) membrane with good integrity can be fabricated from this material, (5) the membrane made of this material should be able to maintain good structural and chemical stability under carbon dioxide pressure gradient, and (6) the sorption and desorption processes in this materials should be fast. The research conducted in this project was to study fundamental issues to understand whether Li_2ZrO_3 meet these three requirements.

It is known that molten carbonate, such as Li_2CO_3/K_2CO_3 can conduct CO_3^{2-} at a very high rate. This is the basis of the molten carbonate fuel cell (MCFC). We also proposed a dual

phase metal-carbonate membrane for high temperature CO_2 separation. This membrane consists of a porous metal phase and a molten carbonate phase, as shown in Figure 2. The metal phase not only serves as a support but also transports electrons. Carbon dioxide separation can be accomplished with the driving force of the CO_2 partial pressure gradient. On the upper stream membrane surface CO_2 , combining with electrons and oxygen, formed $CO_3^{2^-}$, which transports through the molten carbonate phase. The $CO_3^{2^-}$ releases electrons to form CO_2 and O_2 on the downstream membrane surface. The electron transports back, through the metal phase, towards the upstream membrane surface. No external electrodes and connector are required in this dual phase membrane. Since only carbon dioxide (with oxygen) can transport through the molten carbonate, the selectivity for CO_2 over nitrogen or other gases is theoretically infinite.

The dual-phase metal-carbonate membrane is an extension of the fuel cell concept. This

follows the similar approach the inorganic membranologists used for making dense mixedconducting ceramic membranes for oxygen separation, also extended from the concept of the solid oxide fuel cell. The major uncertainty for the successful development of this dual-phase membrane during the Phase I research was whether a hermetic, stable metal-carbonate dual



Figure 2 Membrane Wall Cross-Sectional View Illustrating the Concept of Dual Phase Metal-Carbonate Membrane for High Temperature CO₂ Separation

phase membrane could be fabricated by the direct infiltration method. The research conducted in Phase I was to experimentally verify the synthesis of such dual-phase membrane by a simple synthesis method.

EXPERIMENTAL

We prepared powders of pure lithium zirconate from lithium carbonate and zirconium oxide by a solid-state method. CO_2 sorption properties of the obtained pure Li₂ZrO₃ powders were tested by an electronic microbalance and thermogravimetric analysis (TGA). In synthesis of the dual-phase metal-carbonate membrane, 43.5/31.5/25 mole% Li/Na/K carbonate was used as the molten carbonate. Melting point of Li/Na/K carbonate was 397°C and it has a higher $CO_3^{2^-}$ ionic conductivity than other carbonates [2]. With the lower melting point as compared to other carbonates, Li/Na/K carbonate membrane could be used at temperatures down to about 400°C. Porous 316L stainless steel discs (Series 1000, Media Grade 5) from Mott Metallurgy were used as the membrane substrate. The metal membrane is made by compacting metal particles, and it has an average pore diameter of about 3 µm and porosity of about 40%. The metal-carbonate dual phase membrane was prepared by the direct infiltration coating method. In this method, one surface of the metal membranes was brought in contact with molten carbonate

kept at a temperature above its melting point. Gas tightness of the membranes was checked by the unsteady state helium permeation method.

RESULTS AND DISCUSSION

Lithium Zirconate Particles and Membranes

Figure 3 shows a typical sample weight uptake of the pure Li₂ZrO₃ powder at 500°C after the surrounding gas is switched from the pure dry air to air containing 50% CO₂ ($P_{CO2}=0.5$ atm).

The figure shows a slow but clear increase in the sample weight. XRD and TGA/DSC analyses suggest that the weight increase corresponds to formation of Li₂CO₃ and ZrO₂ through reaction between CO_2 and Li_2ZrO_3 . It is clear from the results given in Figure 3 that pure Li₂ZrO₃ can absorb CO₂ up to around 20 wt% of its sample weight at 500°C within 10.000 min. Although this material has very high CO₂ sorption capacity, the sorption rate is low.

The reaction chemistry and the data of CO₂ sorption and TGA/DSC, XRD and SEM analyses performed in our laboratory suggest the following sorbent microstructure and mechanism for CO₂ sorption on pure Li₂ZrO₃ powder, as shown in Figure 4. The Li₂ZrO₃ powders are



Figure 3 CO₂ uptake curve of pure

made of aggregates of about 10 µm in size. These aggregates consist of many finer Li₂ZrO₃ crystallites of about 0.1-0.5 µm in diameter. When these Li₂ZrO₃ crystallites are exposed to CO₂ at 500°C, CO₂ molecules move to the surface of the Li₂ZrO₃ crystallite and react with Li₂ZrO₃ to form solid ZrO₂ (monoclinic phase) and Li₂CO₃. The initial period of the relative faster increase in the CO₂ sorption uptake may correspond to the carbonation process before the formation of a dense Li₂CO₃ shell on the outer surface and a dense ZrO₂ shell in the middle covering the unreacted Li₂ZrO₃ core, as shown in Figure 4. ZrO₂ and Li₂CO₃ shells are in solid state because their melting points are higher than the temperature for CO₂ sorption (melting point of the Li₂CO₃ and ZrO₂ are respectively 723°C and 2700°C). After the formation of the two Li₂CO₃ and ZrO₂ shells, the carbonation reaction can continue, but at a much slower rate. As shown in Figure 4, CO_2 can diffuse through the solid Li₂CO₃ shell, and react with Li⁺ and O²⁻ on the outer surface of the ZrO₂ shell.

Another reaction occurs on the surface of the unreacted Li_2ZrO_3 to generate Li^+ and O^2 , as indicated in Figure 4. It is well known that ZrO₂ contains a considerable number of defects in its crystals including oxygen vacancy [3, 4]. Oxygen ions can jump through the oxygen vacancy sites and Li⁺ diffuses interstitially through the ZrO₂ shell. The carbonation reaction is limited by the solid state transport of CO₂, Li^+ and O^{2-} in the Li_2CO_3 and ZrO_2 shells. Since the sizes of Li^+ and O^{2-} ions are much smaller than the molecular size of CO₂, the diffusion of CO₂ in the

solid Li₂CO₃ layer is expected to be much slower than the diffusion of Li⁺ and O²⁻ ions in the ZrO₂ shell. Therefore the former is more likely to be the rate-limiting step. The diffusion coefficient of CO₂ in the solid Li₂CO₃ shell, estimated from the CO₂ sorption uptake and particle size, is in the order of 10^{-14} cm²/s at 500°C

We found that the rate of CO_2 sorption on lithium zirconate can be significantly improved by doping about 10 mole% KCO₃ (with respect to LiCO₃). The doped Li₂ZrO₃ can adsorb 20 wt% CO₂ in 200 min, about 50 times faster than the pure Li₂ZrO₃. During carbonation of the doped lithium carbonate the outer shell is LiCO₃-KCO₃ which is molten at 500°C. CO₂ diffuses through the molten carbonate in the case of the doped lithium zirconate, much faster than solid carbonate (pure LiCO₃) in the case of undoped lithium zirconate. These results suggest that the doped lithium carbonate can be a good sorbent for high temperature carbon dioxide separation. However, the membrane made of either pure and doped lithium zirconate would not function properly. A fresh Li₂ZrO₃ membrane, once exposed to CO₂ gradient, will convert to ZrO₂ and lithium carbonate. This initial step during the use of the membrane is accompanied with phase change and structural rearrangement. The membrane cannot maintain the mechanical integrity for continuous separation of carbon dioxide.

Dual-Phase Membranes

The metal-carbonate dual phase membrane was prepared by the direct infiltration coating method. It was important to pre-heat the metal substrate in the same furnace as the carbonate.

Otherwise, a thick dense carbonate layer could be formed on the surface of. inside, the not metal The first dipsubstrate. coating experiment was carried out at 430°C. slightly higher than the carbonate's melting point. The result looked better than the case without preheating the metal substrate. However, there was still a thin carbonate film covering the surface of the metal substrate. Then, the temperature for the carbonate was raised to 500°C to reduce viscosity of the molten carbonate.



Figure 4 Schematic illustration of carbonation mechanism on Li₂ZrO₃ without and with K₂CO₃

Also the metal substrate was pre-heated for longer pre-heating time (15 min) at the same temperature. Good dual-phase metal-carbonate membrane was prepared under these conditions. Visual observation indicates that the pores of the metal membrane were completely filled with

carbonate and there was essentially no carbonate layer covering the metal substrate membrane surface.

The dual-phase membrane was characterized by XRD for phase structure and He permeation for gas-tightness. XRD analysis clearly shows X-ray diffraction peaks of stainless steel and carbonate. Helium permeance through the dual-phase metal and molten carbonate is much lower than 10^{-10} mol/m².s.Pa, more than 6 orders of magnitude lower than that for the original porous metal membrane. This means that the obtained metal-carbonate membrane is very gas-tight and infiltration of metal membrane pore with the molten carbonate was very successful. The infiltrated carbonate can sustain at least 5 bar transmembrane pressure drop. Since helium will not permeate through the membrane and carbon dioxide will transport through the dense molten carbonate by the ionic transport mechanism, the gas-tightness would translate to good permselectivity for carbon dioxide over helium or nitrogen for the dual-phase membrane at high temperatures. Based on the $CO_3^{=}$ conductivity data (electronic conductivity is infinite for metals), it is estimated that CO^2 permeance of about 1×10^{-7} mol/m².s.Pa can be obtained for this membrane at 500-600°C.

PUBLICATIONS FROM THIS PROJECT

The following papers have been prepared summarizing the results obtained from this project:

- 1. J.-I. Ida and Y.S. Lin, "Mechanism of high temperature CO₂ sorption on lithium zirconate", *Environmental Science and Technology*, in press (2003)
- 2. J.-I. Ida and Y.S. Lin, "Synthesis and CO2 Sorption Properties of Pure and Modified Lithium Zirconate", *Separa. Purif. Technol.*, Submitted (2003)
- 3. R. Xiong, J.-I. Ida and Y.S. Lin, "Kinetics of carbon dioxide sorption on potassium doped lithium zirconate", *Chem. Engin. Sci.*, Submitted (2003)

CONCLUSIONS

The results obtained in this project suggest that the doped lithium carbonate can be a good sorbent for high temperature carbon dioxide separation. However, the membrane made of either pure and doped lithium zirconate would not function properly. We succeeded in synthesizing a hermetic, stable metal-carbonate dual phase membrane consisting of a porous metal phase and a dense molten carbonate. Nitrogen or helium is not permeable through these membranes (only CO_2 , with O_2 can permeate through the membrane based on the transport mechanism). Since only carbon dioxide (with oxygen) can transport through the molten carbonate, the selectivity for CO_2 over nitrogen or other gases is theoretically infinite.

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