Novel Ceramic Membrane for High Temperature Carbon Dioxide Separation

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ABSTRACT

A double layer model to describe the mechanism of CO_2 sorption/desorption for both pure and modified lithium zirconate was proposed based on the all data obtained so far with the help of TGA, DSC and XRD analysis. The model can elucidate well the CO_2 sorption/desorption behavior of lithium zircocnate in both pure and modified cases.

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INTRODUCTION

Development of carbon dioxide separation technology from various gas streams at high temperatures (400-700 °C) is very important to the reduction of the carbon dioxide emission to the atmosphere. For example, 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. It is highly desirable to separate CO₂ from flue gas at a high temperature (for example, around 350°C after the economizer) without cooling the flue gas to room or even lower temperature. The high temperature CO₂ separation process would produce concentrated, warm CO₂ which can be subsequently used directly as feedstock for high temperature chemical synthesis of fuels (e.g., methanol or chemicals).

In the above application, incorporation of a high temperature CO_2 separation process would significantly improve the efficiency and economics of overall processes for power generation and carbon dioxide sequestration. Adsorption and membranes are relatively new separation technologies. 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 CO_2 permselective membrane than to prepare a similar sorbent. Various adsorbents for selective sorption of CO_2 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 CO_2 separation.

Phase I research was proposed to develop inorganic membrane for carbon dioxide separation from flue (or coal gasification gas) in the temperature range of $350-550^{\circ}$ C. We conducted many experiments in YEAR I to identify the microstructure and CO₂ sorption mechanism for a unique ceramic material (lithium zirconate) with good properties for CO₂ separation in this temperature range. Based on the results obtained in YEAR I we developed a double layer model to describe the mechanism of CO₂ sorption/desorption for both pure and modified lithium zirconate.

PROPOSED CO2 SORPTION MECHANISM

Based on the all obtained results in Year I research, we proposed a mechanism of CO_2 sorption on pure and modified lithium zirconate shown in Fig. 1. When pure lithium zirconate is exposed to CO_2 at 500°C (Fig.1 (a) to (b)), CO_2 molecules move to the surface of the lithium zirconate and react with lithium zirconate to form solid zirconium oxide (monoclinic phase) and lithium carbonate. The initial period of the relative faster increase in the CO_2 sorption uptake may correspond to the carbonation process before the formation of a dense lithium carbonate shell on the outer surface and a dense zirconium oxide shell in the middle covering the unreacted lithium zirconate core. Zirconium oxide and lithium carbonate shells are both in solid state because their melting points are higher than the temperature for CO_2 sorption. After the formation of the two lithium carbonate and zirconium oxide shells, the carbonation reaction can continue, but at a much slower rate. As shown in Fig.1, CO₂ may diffuse through the solid lithium carbonate shell, and react with Li⁺ and O²⁻ on the outer surface of the zirconium oxide shell. Another reaction occurs on the surface of the unreacted lithium zirconate to generate Li⁺ and O²⁻. It is well known that zirconium oxide contains a considerable number of defects in its crystals including oxygen vacancy (1, 2). Oxygen ions can jump through the oxygen vacancy sites and Li⁺ diffuses interstitially through the zirconium oxide shell. The carbonation reaction is limited by the solid state transport of CO₂, Li⁺ and O²⁻ in the lithium carbonate and zirconium oxide shells. Since the sizes of Li⁺ and O²⁻ ions are much smaller than the molecule size of CO₂, the diffusion of CO₂ in the solid lithium carbonate layer is expected to be much slower than the diffusion of Li⁺ and O²⁻ ions in the zirconium oxide shell. Therefore the former is more likely to be the rate-limiting step.

In the case of modified lithium zirconate (Fig.1 (c) to (d)), mixture of Li/K carbonates layer covering lithium zirconate will be melt and become a liquid layer (this is referred to as a molten carbonate) because of its lower melting point. After that, CO₂ diffuses through the molten carbonate layer and reacts with lithium zirconate. In this case, lithium carbonate formed during the carbonation reaction is mixed with the molten carbonate to increase the volume of the molten carbonate layer. The diffusion of CO₂ in the molten carbonate, with a diffusivity of about 10⁻⁵ cm²/s in 500- 600°C (3-6), is much faster than that in the solid carbonate. This can explain well the higher CO₂ sorption rate in the case of modified lithium zirconate. This suggests that the doped lithium zirconate 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 can not maintain the mechanical integrity for continuous separation of carbon dioxide.

CONCLUSION

In this half year of Year II research, we focused on understanding the CO₂ sorption/desorption mechanism on lithium zirconate. Considering the all obtaied data, we proposed a double layer model to describe the CO₂ sorption/desorption behaviar of lithium zirconatte. In the model, final product after CO₂ sorption is a particle which consist of ZrO_2 core inside and Li_2CO_3 layer. In the pure Li_2ZrO_3 , the formation of solid Li_2CO_3 shell inhibits transport of CO₂, resulting in very slow carbonation rate. On the other hand, doping K_2CO_3/Li_2CO_3 in Li_2ZrO_3 helps trasforming the solid carbonate film to the liquid one during the carbonation reaction. CO₂ diffusion in this liquid (molten) carbonate film is very fast, promoting CO₂ sorption rate considerably.

These results show that Li_2ZrO_3 is potentially an excellent sorbent for separation of CO_2 at high temperature. However, pure Li_2ZrO_3 is not a good material for the CO_2 semi-permeable membrane proposed originally. Nevertheless, the CO_2 sorption and microstructure results of the K_2CO_3/Li_2CO_3 doped Li_2ZrO_3 show that molten carbonate is highly CO_2 semi-permeable. The

molten carbonate, if imbedded in a metal mesh, will give a CO_2 permeability larger than 0.5-2 x10⁻¹¹ mol/m.s.Pa at 600 °C. With these results, we have decided to pursue the direction of preparing high temperature CO_2 perm-selective membrane using the molten carbonate material instead of lithium zirconate. Based on the understanding of CO_2 sorption mechanism for lithium zirconate conducted in Year I of phase I project, we proposed to develop a new CO_2 permselective dense dual-phase inorganic membrane for separation of CO_2 from the flue gas in the temperature range of 350-550°C.

LITERATURE CITED

- (1) R. Stevens, Zirconia and Zirconia Ceramics, Magnesium Elektron Ltd., Twickenham, UK (1986)
- (2) Y.S. Lin, K.J. de Vries, H.W. Brinkman and A.J. Burggraaf, J. Membrane Sci., 66, 211-226(1992)
- (3) P. Claes, B. Thirion and J. Glibert, Solubility of CO₂ in the Molten NaCO₃-K₂CO₃ (42mol%) Eutectic Mixture at 800 °C, Electrochimica Acta, 41 (1996) 141-146.
- (4) P.L. Spedding and R. Millis, J. Electrochem. Soc., 113, 559 (1965).
- (5) P.L. Spedding and R. Millis, J. Electrochem. Soc., 113, 594 (1965).
- (6) P.L. Spedding, J. Electrochem. Soc., 117, 177 (1970).



Fig.1 Schematic illustration of carbonation mechanism on pure and modified Li₂ZrO₃